



Rotational population distribution of KH (v=0, 1, 2, and 3) in the reaction of K(52 P J , 62 P J , and 72 P J) with H2: Reaction mechanism and product energy disposal

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Rotational population distribution of KH (v=0, 1, 2, and 3) in the reaction of K(5 ${}^{2}P_{J}$, 6 ${}^{2}P_{J}$, and 7 ${}^{2}P_{J}$) with H₂: Reaction mechanism and product energy disposal

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Using a pump-probe method, we have systematically studied the rotational distribution of KH (v=0-3) produced in the reaction of K (5P, 6P, and 7P) with H₂. The resulting rotational states fit roughly a statistical distribution at the system temperature, while the vibrational populations are characterized by a Boltzmann vibrational temperature of 1800, 3000, and 3100 K for the 5p, 6P, and 7P states, respectively. These results provide evidence that the reaction follows a collinear collisional geometry. This work has successfully probed KH from the K(5P) reaction, and confirms that a nonadiabatical transition via formation of an ion-pair $K^+H_2^-$ intermediate should account for the reaction pathway. The available energy dissipation was measured to be $(68\pm4)\%$, $(26\pm2)\%$, and $(6\pm3)\%$ into the translation, vibration, and rotation of the KH product, respectively. The energy conversion into vibrational degree of freedom generally increases with the principal quantum number, indicating that the electron-jump distance elongates along the order of 5P < 6P < 7P. The result is different from the $Cs(8P,9P)-H_2$ case, in which the electron-jump distances were considered roughly the same. Furthermore, a relatively large distance is expected to account for highly vibrational excitation found in the KH product. According to the classical trajectory computation reported by Polanyi and co-workers, the strong instability of the H_2^- bond, inducing a large repulsion energy, appears to favor energy partitioning into the translation. © 1996 American Institute of Physics. [S0021-9606(96)01443-2]

I. INTRODUCTION

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The simplicity of a three-atom reaction scheme,

$$\mathbf{A} + \mathbf{H}_2 \rightarrow \mathbf{A} \mathbf{H} + \mathbf{H},\tag{1}$$

is next to the case of $H+H_2 \rightarrow H+H_2$ and its isotopic variants. The information related to Eq. (1) may provide insight into the dynamical behavior of more complicated systems. To overcome the endoergicity involved, the method of energy disposal in the atomic reactant with a tunable radiation source is feasible and widely employed. The cases, which have been under investigation, include nonmetal atoms such as C¹, O², and F (Ref. 3) as well as metal atoms such as Na⁴, K,⁵ Cs,⁶ Hg,⁷ Zn,⁸ and Cd.⁸ Among the courses of dynamical complexity studied, the reaction pathway is an issue of common concern. To achieve this goal, measurements by crossed molecular beams,^{3,6} isotope effects,^{9,10} and spectroscopic methods^{1,2,8} are frequently adopted. In the crossed-beam experiment, the scattering distribution of the product with respect to the center of mass of the system is correlated with a direct or indirect reaction mechanism. With the use of HD as a reactant, information on the H/D ratio may imply intermediate geometry. If the ratio is larger than unity, an insertive reaction is preferred. Otherwise, the reaction may preferentially proceed via an abstraction mechanism.⁹ Note that in some nonadiabatic reaction mechanisms, more complicated parameters determine the isotope effect, such that the simple indication may fail.^{4,11} Spectroscopic analysis of the rovibrational state distribution of the product is also indicative of the reaction mechanism. A bent-geometric insertion usually leads to a product accompanied by hot rotation and cold vibration, whereas a collinear abstraction reaction leads to a product with cold rotation and hot vibration. For many complicated systems, however, potential energy surface and trajectory computation should be considered to gain full insight into the reaction complexity.

Although the collisions of excited alkali atoms with H_2 have been investigated for decades, the related reaction dynamics is not well understood. For instance, the argument was once focused on whether a single collision between Cs(7P) and H_2 could produce CsH.^{6,12–15} Sayer and coworkers provided a model for the CsH formation via a secondary collision through either the vibrationally excited H_2 or $(CsH_2)^*$ as a mediate step.^{12,13} In contrast, Vetter and co-workers measured the CsH product with two crossed molecular beams, which ensured that the observation was under a single-collision condition.^{6,14,15} They demonstrated that the reaction cross section for $Cs(7P_{1/2})$ was larger than $Cs(7P_{3/2})$, despite a larger energy disposal in the latter reactant. They also expected that CsH was formed in a collinear collision via an electron harpoon mechanism. Since the sys-

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tem energy is just over the reaction threshold, only the ground vibrational state of CsH can be observed, but the information on extra energy partitioning is not available. In a very recent study with Cs 8*P* and 9*P* atoms as reactants, Bersohn and co-workers reported that the vibrational state v=1 of CsH could be observed, and about 90% available energy was released as translation.¹⁶ A collinear geometric collision was anticipated to cause the CsH product, but the electron transfer occurred at a shorter distance between Cs and H₂ than the harpoon model predicted. Due to similarity of the product rovibrational distributions between the Cs(8*P*) and Cs(9*P*) reactants, their nonadiabatic surface crossings were almost at the same region.

The nonreactive behavior of $Na(3P) + H_2$ is well understood, but the reaction behavior for the excited Na atom has seldom been studied. In a recent study on the reaction of Na(4P) with H₂, Bililign and Kleiber¹¹ found that (1) a bimodal rotational distribution of NaH resulted with the minor component peaking at low J and the major component peaking at high J; (2) there was no kinematic isotope effect on the rotational distribution. Accordingly, the bimodal nature was anticipated to originate from a side-on attack along an attractive surface, which determined the microscopic branching late in the exit channels. A similar model was previously proposed by Breckenridge et al. to account for the rotational bimodality found in the Mg(${}^{1}P_{1}$)-H₂ reaction.¹⁷ However, in measuring far-wing absorption profiles of the NaH₂ collision complex, the blue-wing detuning was found to favor low rotational states of the NaH product, while the red-wing detuning leaded preferentially to high rotational states.⁴ This suggests that the reaction may also proceed via a second pathway. That is, an impulsive end-on attack mechanism along a repulsive surface probably results in NaH, with low rotational excitation. On the other hand, the theoretical work of Sevin and Chaquin indicates that the Na(4P)-H₂ reaction mechanism follows an attractive $3^{2}B_{2}$ surface, which evolves through a series of surface crossings and finally joins to the reactive $1^{2}B_{2}$ surface, correlating with the lowest ${}^{2}P$ state of Na.¹⁸

We have studied the reaction of K(7S) and H_2 , observing the resultant nascent KH product with low rotational and high vibrational states.⁵ The reaction mechanism was anticipated to follow a collinear geometry via an electron harpoon process, by analogy with the Cs case. In addition, KH can be state-selectively produced by K(7S) but not by K(5D), despite a similar energeticity shown by these two states. The symmetry correlation between the reactants and the products was considered to appropriately account for the reactivity discrepancy. So far, K(7S) state has been the only state studied that successfully produces KH. Lin, Schilowitz, and Wiesenfeld previously studied collisional deactivation of K(5P)by H₂, but failed to observe any KH product.¹⁹ This system is exothermic by 9 kcal/mol. The lack of KH detection was ascribed to an adiabatic transition, in which the $K(5P) + H_2$ reactants is correlated with the KH* $(A^{1}\Sigma^{+})$ +H products, and the states are energetically inaccessible. In the light of the K(7S)-H₂ reaction,⁵ however, the proposed mechanism for the $K(5P)-H_2$ collision seems questionable. We decided it



FIG. 1. Schematics of pump-probe apparatus.

was worthwhile to repeat this experiment, but using a more sensitive pump-probe technique with a laser-induced fluorescence (LIF) detection. In this manner, we found for the first time the KH product, which resulted from the single collision between K(5P) and H_2 . In addition, we systematically studied a series of K(nP) (n=5, 6, and 7) reaction with H_2 in attempt to clearly understand the reaction pathways and the energy partitioning involved.

In this work, we present a detailed nascent rotational distribution of KH resulting from K(nP) (n=5, 6, and 7). The obtained KH spectra extend to a more complete wavelength range than ever before.⁵ The resulting rotational states suitably fit a statistical thermal distribution, while the vibrational population was highly excited to at least v=3. Accordingly, we confirmed that KH was produced by a collinear H-abstraction reaction via a harpoon mechanism. The available energy dissipation was measured to be 68%, 26%, and 6% into translation, vibration, and rotation of the KH product, respectively. Most available energy was released as translation; the case is similar to the recently reported CsH product. A detailed interpretation on the reaction pathway and energy partitioning will be discussed.

II. EXPERIMENT

A pump-probe technique, as depicted in Fig. 1, has been illustrated elsewhere,^{5,11,17} so only a brief description is stated below. One Nd:YAG laser-pumped dye laser was used as the pump source. The 5*P* state of the K vapor was excited at 404.4 nm with the mixed laser dyes of LD 390 and stilbene 420 in a volume ratio of 4:1. The 6*P* and 7*P* states were prepared with LDS 698 and DCM, respectively. But the output wavelength from the dye laser needed to be frequency-doubled through a KDP crystal emitting at 344.6 and 321.7 nm for excitation of 6*P* and 7*P* state, respectively. The unfocused beam was collimated through a pinhole of ~0.3 cm² cross section with energy output less than 100 μ J, small enough to avoid occurrence of optical saturation or multiphoton absorption process.

The second dye laser pumped by the other Nd:YAG laser was used to probe the LIF spectra of the KH product in the $A^{1}\Sigma^{+}-X^{1}\Sigma^{+}$ transition. The time delay between pump and probe laser, controlled by a delay generator, was adjusted to be about 10 ns. The delay time was short enough to ensure that the product distribution could be considered in a nascent state. The unfocused probe beam was collimated through a pinhole of ~0.3 cm² cross section, propagating opposite with respect to the pump beam. The output energy was kept less than 100 μ J to prevent the obtained LIF spectra from optical saturation.

For achieving a better spectral resolution and signal to noise ratio, appropriate pairs of excitation and emission bands were selected for the various vibrational states. In this work, we selected the pairs of [(v', v'')=(7,0),(7,1)], [(7,1), (7,1)], [(7,(7,0)], [(5,2), (5,0)], and [(6,3), (6,1)], respectively, for probing population at v = 0, 1, 2, and 3. Coumarin 480, coumarin 500, rodamine 575, and a mixture of rodamine 590 and rodamine 610 in a volume ratio of 1:1 were the dyes used for the corresponding vibrational states. The obtained LIF signal of KH was transmitted through a monochromator and detected by a photomultiplier tube enclosed in a cooler at -20 °C. The monochromator with dispersion of 18 A/mm allowed for spectral transmittance of 14.4 nm. The monochromator functioned as a filter to reduce interference of scattered light. The detected signal was fed into a boxcar integrator for signal improvement. By adjusting the delay time appropriately, one could reduce the atomic emission interference to the minimum extent, such that the signal to noise ratio for the LIF spectra may be enhanced. Note that each LIF spectra was recorded over a wavelength range of 15 nm to cover complete rotational states populated. Thus the grating setting in the monochromator had to change positions to record such long wavelengths. The segment of spectra obtained in a respective fixed grating position overlapped each other for more than 5 nm, and then normalized to the identical condition of detection system.

A six-armed heat pipe was used to deposit the K metal, allowing for spectral observation at 90° with respect to the incident laser beam axis.²⁰ A thermocouple was intruded in the vicinity of the reactive regime to monitor the system temperature within an accuracy of ± 1 K. The K metal in the oven was heated to 500 K, yielding a vapor pressure of about 100 mTorr. The chamber was evacuated to 10^{-5} Torr prior to introduction of H₂. The H₂ gas, regulated at a constant pressure of less than 5 Torr which was monitored by a MKS capacitance gauge, flowed slowly through the chamber. Since occurrence of "laser snow" (the KH product) will gradually reduce H₂ pressure, a closed static system may otherwise cause significant error. Also, the chamber needs to be cleaned frequently to prevent a great amount of KH accumulation.

III. RESULTS

A portion of excitation spectra of KH (7,0), (7,1), and (6,3) bands in the $A^{1}\Sigma^{+}-X^{1}\Sigma^{+}$ transition are shown in Fig. 2, as the 5*P*, 6*P*, and 7*P* states of the K atom are excited,

respectively, at 404.4, 344.6, and 321.7 nm. The obtained LIF spectra are under the nascent conditions. For evidence of this fact, we measured the H₂ pressure dependence of KH (7,0)P9, P10, R10, and R11 rotational branch lines at time delay of 20 ns between pump and probe lasers. The results show a linear relationship, which indicates that the reaction under the appropriate H₂ pressure and delay time can be free from interference of rotational cooling. One example for R11 branch line is given in Fig. 3. Assuming the collisional cross section of 10 Å² and the averaged relative speed of 2.4×10^3 m/s, the estimated probability for KH to encounter a secondary collision is less than 0.26 for the condition of 5 Torr H_2 pressure and 10 ns delay time. Thus the resulting distribution was partially disturbed by a secondary collision. In the measurement of the delay time dependence, the relative intensities of overall signals in the varied distributions resembled each other within 20 ns, but the related signal to noise ratio for a brief delay time was poor. This fact indicated that the rotational relaxation was negligible, and the obtained rotational distribution can be reasonably considered to be in a nascent state.

We adopted the molecular constants reported by Stwalley and co-workers for the spectrum assignment.²¹ Since the rotational lines from varied vibrational states happen in the same LIF spectra region, spectra identification becomes complicated. To confirm the assignment's reliability, a relaxed spectra under high pressure H₂>60 Torr and delay time of 300 ns was taken. As reported previously,⁵ the resulting excited vibrational states were quenched, and thus the rotational spectra became ready to be identified. Alternatively, by choosing an appropriate combination of excitation and emission bands, one may reduce the spectral complication to the minimum extent and facilitate identification of a particular vibrational state. For instance, for monitoring the v=3 state, we selected the (6,3) and (6,1) band as the excitation and emission band, respectively. In this combined spectral detection, as shown in Fig. 2(a), only high J levels of v=0, 1, and 2 may appear simultaneously in the same wavelength region, but their intensities are weak. In this manner, we could record the rotational levels, J=0-19, for vibrational states of 0 and 1, and rotational levels up to 14 for v = 2 and 3. The assigned rotational line deviates from its theoretical counterpart within 1 cm⁻¹. K₂ spectral interference with a relatively small rotational constant is free from the spectral region studied. Although population at v = 4 was not probed, we anticipate that some unassigned rotational lines in the (6,3) band might result from this state, especially for the K(6P) atom.

By taking into account Franck–Condon and Hönl– London factors, the rotational quantum state distributions of KH (v=0, 1, 2, and 3) for the K 5*P*, 6*P*, and 7*P* states are displayed in Figs. 4–6. The Franck–Condon factors are adopted from the results by Pardo *et al.*,²² which exhibit agreement with the data we conducted using the INTENSITY program developed by Stwalley and co-workers.²³ For evidence of a reliable nascent rotational distribution, the *R* branch lines of (5,0) and (7,0) bands were monitored and



FIG. 2. Portions of LIF spectra of KH in the $A^{1}\Sigma^{+}-X^{1}\Sigma^{+}$ transition. (a) Excitation of (6,3) band for K(5*P*); (b) excitation of (7,1) band for K(6*P*); (c) excitation of (7,0) band for K(7*P*).

resulted in a consistent distribution for v=0 state. Analogously, the *R* branch lines of (7,1) and (8,1) bands were probed together to give rise to the KH (v=1) population distribution. The population in v=3 for K(7*P*) is not avail-

able, since the signal was buried in the atomic spectral interference from the pump laser. For ease of comparison, all the rotational distributions are represented with the *R* branch lines. The distributions thus obtained for v=0, 1, 2, and 3



FIG. 3. H_2 pressure dependence of the KH (7,0)*R*11 rotational branch line at time delay of 20 ns between the pump and probe lasers.

states appear to be monomodal, peaking in J=7-8. The rotational population profile is roughly consistent with a statistical distribution at the system temperature. A plot of line intensity against J(J+1) yields a slope corresponding to a rotational temperature of 585 ± 65 K, as shown in Fig. 7. The rotational temperature was close to the system temperature, but the fraction of total available energy into the rotation was far from a prior rotational distribution of 2/7. For this reason, a cold rotation is sometimes called from the point of view of the energy disposal, which will be discussed in the next section. The sum of each integrated rotational line equals the population of the corresponding vibrational state. The vibrational populations were characterized by a Boltzmann vibrational temperature of 1712 ± 55 , 3010 ± 124 , and 3127 ± 138



FIG. 5. Rotational quantum state distribution of KH (v = 0, 1, 2, and 3) produced in the reaction of K(6 ${}^{2}P_{J}$) with H₂.

K for the 5*P*, 6*P*, and 7*P* states, respectively. The results are shown in Fig. 8. The total available energy for dissipation is 10.84, 23.73, and 29.59 kcal/mol for the 5*P*, 6*P*, and 7*P* states. Note that the values are estimated by adding a term 5/2kT to the exothermic energy. The fraction of the energy release as rotation, vibration, and translation are listed in Table I.

In this work, we only studied the reaction of the K $P_{3/2}$ state and neglected the spin-orbit effect, which had no evidence showing any difference in the product rotational distributions in the Na(4*P*) and Cs(8*P* and 9*P*) reactions. In fact, the cross section of fine-structure mixing induced by H₂ for the K 5 ${}^{2}P_{J}$ doublets has been measured to be 134 Å² for the transition 5 ${}^{2}P_{3/2}$ —5 ${}^{2}P_{1/2}$ and 72 Å² for its reverse



FIG. 4. Rotational quantum state distribution of KH (v = 0, 1, 2, and 3) produced in the reaction of K(5 ${}^{2}P_{J}$) with H₂.



FIG. 6. Rotational quantum state distribution of KH (v = 0, 1, and 2) produced in the reaction of K(7 ${}^{2}P_{J}$) with H₂.



FIG. 7. Plot of $\ln[I_i/(2J+1)]$ as a function of J(J+1) for the reactions of K5P (a), 6P (b), and 7P (c) with H_2 , respectively. The slopes of the graphs are characterized by the Boltzmann rotational temperature.

process.²⁴ Such large mixing cross sections may have caused the distributions of overall signals being in the statistical 2:1 ratio.

IV. DISCUSSION

A. Collinear geometry

The nascent rovibrational distributions of KH produced by K 5P, 6P, and 7P states with H₂ collision were investigated systematically for the first time in this work. The rotational distributions of KH for various vibrational states are similar, giving rise to a low rotational temperature equivalent to the system temperature. In contrast, the vibrational populations are markedly excited. The observation of hot vibration (temperature of 1700-3100 K) and low rotation (temperature of 585 K) suggests that the reaction follows preferentially a collinear geometric collision.

Using a similar pump-probe method, a previous work on K(7S) with H₂ reaction, which is exothermic by 26 kcal/ mol, also led to KH under a single collision condition.⁵ Analogous to the case of Cs(7P),⁶ a collinear approach to



FIG. 8. Plot of $\ln(I_n)$ as a function of vibrational energy G_n for the reaction of K5P, 6P, and 7P with H₂, respectively. The slopes are characterized by the Boltzmann vibrational temperature.

form an intermediate ion pair of K⁺H⁻H was suggested. Since the rotational spectra covered an incomplete wavelength range of only 63 cm⁻¹, the previous report fell short of information on the precise rotational population distributions of KH for various vibrational states. The present work provides further evidence that a collinear reaction is more plausible for the K case.

The reaction of K(5P) with the H₂ state was previously investigated,¹⁹ using a photolysis laser to produce K(5P)following KI photodissociation at 193 nm, in which the K fragment was predominantly partitioned to the $5^{2}P_{I}$ state.^{19,25} Upon photolysis, the atomic resonance absorption spectra of population relaxation from this state were measured with and without the H₂ mixture. The subsequent spectra appeared to be identical, suggesting that the channel of chemical reaction was negligible. The lack of KH detection was ascribed to an adiabatic transition. The present pumpprobe measurement using LIF detection proved to be more sensitive than that adopted previously. In addition, our work demonstrates that KH should be produced through a nonadiabatic transition, in which the harpoon mechanism forming a K⁺H⁻H ion-pair intermediate is anticipated.

TABLE I. Disposal of available energy in reactions of K(nl) with H_2 .

K(nl)	$5 {}^{2}P_{J}$	$6 {}^2P_J$	$7 {}^2P_J$
E_{AVL} (kcal/mol) ^a	10.84	23.73	29.59
$\langle E_V \rangle$ (kcal/mol)	3.01	5.65	8.14
$\langle E_R \rangle$ (kcal/mol)	0.93	1.04	0.97
$\langle f_v \rangle^{\rm b}$	0.27	0.24	0.28
$\langle f_R \rangle$	0.09	0.04	0.03
$\langle f_T \rangle^{\rm c}$	0.64	0.72	0.69

 $^{\mathrm{a}}E_{\mathrm{AVL}} = -\Delta H + 5/2kT.$

$${}^{\mathrm{b}}\langle f_{v} \rangle = \langle E_{v} \rangle / E_{\mathrm{AVL}}; \langle f_{R} \rangle = \langle E_{R} \rangle / E_{\mathrm{AVL}}.$$

$${}^{\mathrm{c}}\langle f_{T} \rangle = 1 - \langle f_{v} \rangle - \langle f_{R} \rangle.$$

In the case of Na(4P) with the H₂ reaction, the rotational distribution of NaH exhibits bimodality.^{4,11} Bililign and Kleiber suggested that the major reaction pathway proceeds via a bent collisional geometry with Na-insertion into the H_2 bond, leading to the branching of low J and high J components late in the exit channel. The bent NaH₂ intermediate may be partially stabilized through the electron donation between the metal and the unfilled antibonding of H_2 . Similar interpretation was adopted in the $Mg(3P)-H_2$ reaction for the MgH₂ stabilization.¹⁷ In contrast, in the case of K or Cs, the center H⁻ of the ion-pair intermediate functions analogously as a divalent element, such as Be. According to the valence shell electron pair repulsion (VSEPR) model, a linear geometry might be the best structure to reduce the repulsive interaction between the metal and the end H atom to the minimum extent. Alternatively, Bersohn and coworkers suggested that the atomic size might determine the collisional geometry.¹⁶ K and Cs, which have a larger size than Li and Na may encounter a repulsive force in an insertive approach, and thus a collinear reaction is preferentially obeyed. In their study on the Cs 8P and 9P state, Bersohn and co-workers concluded that a collinear reaction between the reactants is preferred as a result of cold rotation found in CsH. The result confirms the mechanism proposed by Vetter and co-workers in a crossed-beam experiment of Cs(7P)and H₂.⁶ Some theoretical results also lend support to such a collinear reaction mechanism. For instance, the theoretical work by Gadea *et al.* predicted that the Cs(7P)-H₂ reaction proceeds via a collinear ion-pair intermediate with the 7Pelectron jumping on the H₂ system at a harpoon distance of 6 bohr.^{26,27}

B. Harpoon mechanism

The reactions of K and Cs with H₂ favor a nonadiabatic transition through an ion-pair intermediate, although Bersohn and co-workers¹⁶ suggest that the electron transfer occurs within a shorter distance than predicted by the harpoon model. Alternative evidence for the fit of the harpoon mechanism to our case is provided elsewhere.²⁸⁻³⁰ In the measurement of total cross section of collisional deactivation for $K(n^2S, n=7-11)$ by H₂, the resulting value increases abnormally with principal quantum number.²⁹ The cross section of 7S, 8S, and 9S, for instance, were measured to be 150 ± 2 , 167 \pm 5, and 189 \pm 9 Å^{2,29} The obtained values are much larger than those predicted by the hard sphere model. In contrast, K-rare gas collisions yield values of 32±4, 35±2, and 56 ± 3 Å² for the corresponding state as quenched by Ar.³⁰ H₂ and rare gas are regarded as the inefficient quencher towards the lower excited alkali atoms, for their lowest unoccupied molecular orbitals belonging to σ^* symmetry.³¹ The abnormal quenching behavior reflected in the H₂ collision of a highly excited K atom is caused by a long-range electron transfer. The collision complex hops to the ionic surface, which crosses several lower K-H₂ covalent surfaces as the exit channels. The probability for the nonadiabatic curve crossing may be estimated by the Landau-Zener theory. The exit into the physical quenching channel seems to dominate

TABLE II. Symmetry correlation among reactants, ion-pair intermediates, and products for varied geometric approaches.

	Symmetry		
System	$C_{\infty v}$	C_s	C_{2v}
$ \begin{array}{l} K(n^2S) + H_2(X^1\Sigma_g^+) \\ K(n^2D) + H_2(X^1\Sigma_g^+) \end{array} $	Σ^+ Σ^+ 2 Π	A' 3A' 2A"	$\begin{array}{c} A_1 \\ 2A_1 \\ A \end{array}$
	2Δ	ZA	$ \begin{array}{c} A_2 \\ B_1 \\ B_2 \end{array} $
$\mathrm{K}(n^2 P) + \mathrm{H}_2(X^1 \Sigma_g^+)$	${\Sigma^+\over 2\Pi}$	2A' A''	A_1 B_1 B_2
	$rac{\Sigma^+}{\Sigma^+}$	A ' A '	$\begin{array}{c} A_1 \\ A_1 \\ A_1 \end{array}$

the total deactivation processes. For evidence of this, in the nonreactive measurement of the K 7*S* state by H₂, the total deactivation cross section was dominated by the 7S-5D state-to-state transition.²⁸ Analogously, the total deactivation process of the K 5*P* state by H₂ was dominated by the 5*P*-(3*D*,5*S*) state-to-state exit channel.¹⁹ Although the reaction cross section has not been measured yet, the corresponding value should be relatively small because of the measurement for the state-to-state deactivation cross section. A known reaction cross section may be found in the Cs(7*P*)–H₂ collision,^{6,32} yielding an expectably small value. The fact was interpreted as arising from at least five states in between interacting with the ionic curve competes with the reaction channel.

According to the harpoon model, the crossing region between the ionic potential surface and the covalent potential surface should be located in the long-range attractive portion. In previous work on the K(7S) atom, the crossing location corresponded to 4.1-4.8 Å, and the activation energy of the reaction was determined to be 2-3 kT.⁵ This small potential barrier fits the conditions required for the harpoon mechanism. The term energies for the *nP* states studied are comparable to the K(7S) state; therefore, we expect that the surface crossing is analogously located in a long-range region, and the reaction should encounter the least activation barrier.

In the harpoon mechanism, a linear ion-pair K⁺H⁻H intermediate may symmetrically correlate with the $K(^{2}P)$ and $H_2({}^{1}\Sigma_{g}^{+})$ reactants and with the $KH({}^{1}\Sigma^{+})$ and $H({}^{2}S)$ products through the Σ^+ symmetry. The symmetry correlations associated with reactant, intermediate, and product for different angular quantum states are listed in Table II. In the C_{mn} symmetry, a fraction, which is associated with the covalent surface effectively undergoing a nonadiabatic transition, is 1, 1/3, and 1/5 for the S, P, and D orbital, respectively. In other words, the feasibility of producing KH from different atomic orbital follows the order of D < P < S, assuming similar term energies are involved. The trend is consistent with the prediction by Bersohn and co-workers,¹⁶ adopting the concept of electronic wave function for the high-lying atomic state. They interpreted that the extent of wave function penetration near the atomic nuclear core is along the order of $D \le P \le S$,

and the feasibility of electron transfer depends on the mutual wave function overlap. Accordingly, the probability for surface hopping follows the same trend.

C. Energy partition

Among the reactions of K 5P, 6P, and 7P states with H₂, the determined values of energy partitioning into translation, vibration, and rotation of KH are roughly the same, giving results of 0.68±0.04, 0.26±0.02, and 0.06±0.03, respectively. However, when considering individual vibrational degrees of freedom, one may find that the 5P, 6P, and 7P state has an energy disposal of 3.01, 5.65, and 8.14 kcal/ mol, respectively. This fact suggests that the surface crossing region gradually increases with increase of the principal quantum number, which agrees with the harpoon model. On the other hand, the rotational energy conversion extent is almost the same, irrespective of the varied P states, suggesting that a collinear reaction can be effectively applied to all the *P* states studied. In contrast, the total available energies dissipated into the CsH vibration were roughly the same in both Cs 8P and 9P states. Electron transfer at an almost equal distance between the Cs atom and H₂ was thus suggested.¹⁶

By analogy with the Cs (8P,9P) and H₂ system, most available energy, of about 70% in the K-H₂ collision, was dissipated into translation. Therefore, one may expect that the ion-pair formed in the electron transfer has no time to adjust the H₂⁻ bond distance prior to dissociation. The instability of H_2^- , which is restricted to a H_2 bond distance of 0.74 Å, breaks the bond abruptly, and the impulsive energy released is thus mostly changed to translation. Due to a short lifetime compared to the rotational period, the dissociation of ion-pair intermediate cannot lead to an isotropic product distribution, as has been revealed in a crossed-beam experiment by Vetter and co-workers.¹⁴ They found that CsH scattered in a forward direction relative to the incident Cs atom. We expect a similar phenomena will be observed in our case.

In an electron-harpoon reaction $M+X_2 \rightarrow M^+X_2^ \rightarrow$ MX+X, the product energy distribution among various degrees of freedom is closely related to the electron-jump distance, the repulsive force for breaking the X_2^- bond, the incident collision angle, the initial kinetic energy, and the mass effect. Polanyi and co-workers have thoroughly investigated such a reaction using a classical trajectory method on an appropriate ionic potential energy hypersurface of $M^+X_2^-$.^{33,34} Based on their computations, we have attempted to compare the behavior of energy distributions among the three cases $K+Br_2$,³⁵ K^*+H_2 , and Cs^*+H_2 .¹⁶ The products of these reactions are commonly characterized by a collinear approach through an ion-pair intermediate. However, the product energy partitioning into various degrees of freedom is remarkably different, especially for vibration and translation. For instance, the fraction $E_{\rm vib}/E_{\rm tot}$ was measured to be >60%, 25%, and 10% for K-Br₂, K-H₂, and Cs-H₂. E_{vib} and E_{tot} denote the vibrational energy and the total available energy. In the reaction of L+HH (L, light atom; H, heavy atom), when the attacking atom is light along a collinear approach, the new bond LH tends to be formed before the HH repulsion completely dissipates. In contrast, for the H+LL type, the bond forming and breaking occur simultaneously. That is, during the energy release of LL bond breaking, the new bond HL is still forming. Accordingly, when the halogen molecules are replaced by the hydrogen molecule, the fraction $E_{\rm vib}/E_{\rm tot}$ is expected to increase, if all other conditions remain the same.³³ Observations of the K-Br₂ and K-H₂ cases seem to go against the mass effect prediction. The discrepancy might be interpreted as arising from the difference between the repulsion of Br_2^- and H_2^- , which is estimated by the bond dissociation energy to be 1.15 eV and 4.78 eV.³⁶ (The electron affinity of H_2 is not taken into account.) According to classical trajectory computations,³³ the $E_{\rm vib}/E_{\rm tot}$ tends to decrease with increasing the repulsion of X_2^- . In the cases of K or Cs, the strong instability of the $H_2^$ bond apparently favors the energy partitioning into the translation. Alternatively, due to the large electron affinity of Br₂ relative to H₂, a larger electron-jump distance in the K-Br₂ reaction may also partially enhance vibrational excitation.

We now attempt to interpret the difference of translational energy partitioning between K-H₂ and Cs-H₂. If the electron-jump distance is kept constant, the fraction $E_{\rm vib}/E_{\rm tot}$ is anticipated to increase as the mass of attacking atom increases.³³ However, the experimental data disagree with the prediction. The contradictory observation implies that the Cs-H₂ should have a shorter electron-jump distance, so that the vibrational energy partitioning will be reduced. This consideration is supported by the findings of vibrational states up to only one for the $Cs(8P,9P)-H_2$ reaction, but up to at least three for the K(5P, 6P, 7P) case. Such prediction for the Cs case is consistent with the report by Bersohn and co-workers.

V. CONCLUSION

We have systematically studied the rotational distribution of KH (v=0-3) in the reaction of K(5P, 6P, and 7P) with H₂. The spectroscopic analysis indicates that the rotational populations are in the statistically thermal distribution, irrespective of varied vibrational and electronic states. These results provide further evidence that the reaction follows a collinear collisional geometry. This work has successfully probed KH produced in the K (5P) reaction, and confirms that a nonadiabatical transition via formation of an ion-pair $K^+H_2^-$ intermediate should account for the reaction pathway. The fraction of product energy partitioning yields 68%, 26%, and 6% for translation, vibration, and rotation. The energy conversion into vibration generally increases with the principal quantum number, indicating that the electron-jump distance elongates along the order of 5P < 6P < 7P. The subject reaction can be regarded as the type H+LL (L, light atom; H, heavy atom), in which the HL is still forming during the energy release of LL bond breaking. The case differs from the type of L+HH, in which most energy is deposited in the vibration. In the K-H₂ reaction, the strong instability of the H_2^- bond favors the energy partitioning into the translation. As compared to the Cs-H2 case, relatively large

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