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Dynamics of OH and OD radical reactions with HI and GeH_4 as studied by infrared chemiluminescence of the H₂O and HDO products

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The infrared chemiluminescence of vibrationally excited H₂O and HDO from the highly exothermic reactions of OH and OD radicals with HI and GeH_4 was observed in the 2200–5500 cm⁻¹ range. The experiments utilized a fast-flow reactor with 0.3-1 Torr of Ar carrier gas at 300 K; the OH(OD) radicals were produced via the $H(D)+NO_2$ reaction and the H or D atoms were generated by a discharge in a $H_2(D_2)/Ar$ mixture. The H_2O and HOD vibrational distributions were determined by computer simulation of the emission spectra in the 2200-3900 cm⁻¹ range. The total vibrational energy released to H₂O and HOD molecules is, respectively, $\langle f_n \rangle = 0.36$ and 0.41 from HI and $\langle f_v \rangle = 0.46$ and 0.51 from GeH₄. These values are significantly smaller than for the reactions of OH and OD with HBr, $\langle f_v \rangle = 0.61$ and 0.65. The populations of the O–H stretching vibration of HOD and the collisionally coupled ν_1 and ν_3 stretching modes of H₂O decrease with increasing vibrational energy. In contrast, the vibrational distribution from the HBr reaction is inverted. The bending mode distributions in all stretching states of H₂O and HOD extend to the thermodynamic limit of each reaction. A surprisal analysis was made for H₂O(HOD) distributions from the title reactions and compared with that for OH(OD)+HBr. The surprisal analysis tends to confirm that the dynamics for the HI and GeH₄ reactions differ from the HBr reaction. The HI reaction may proceed mainly via addition-migration, while the GeH_4 reaction may involve both direct abstraction and addition-migration. A rate constant for the $OH+GeH_4 \rightarrow H_2O+GeH_3$ reaction was evaluated by comparing the H₂O emission intensities with that of the OH+HBr \rightarrow H₂O+Br reaction, $k_{\text{GeH}_4}/k_{\text{HBr}} = 6.5 \pm 0.9$. Secondary kinetic-isotope effects, $k_{\text{OH}}/k_{\text{OD}} = 1.4 \pm 0.1$, 1.0 ± 0.2 , and 1.3 ± 0.2 , were determined for reactions of OH and OD with GeH₄, HI, and HBr, respectively, by comparing the relative H₂O and HOD emission intensities. © 1997 American Institute of Physics. [S0021-9606(97)00411-X]

I. INTRODUCTION

Hydroxyl radical reactions are important from both practical and fundamental points of view. Practical applications include combustion and atmospheric chemistry and involve reactions with a wide range of organic and inorganic molecules and radicals. On the theoretical side, the abstraction reactions giving H₂O provide the opportunity to study the formation of a triatomic product molecule in specific quantum states. In particular, the reactions of OH with hydrogen halides have been extensively studied to provide a kinetic database for atmospheric chemistry^{1,2} and hydrocarbon combustion.³ Reaction rates also have been studied for deuterium halides⁴⁻⁷ and vibrationally excited hydroxyl radicals.^{6,7} In contrast to the kinetics, very little is known about the dynamics of these important reactions, and only the first efforts are being made to determine the energy disposal and to explain the unusual temperature dependence of the rate constants.⁸⁻¹⁰ The infrared chemiluminescence technique has been successfully used to study the dynamics of the H atom abstraction reactions by O, F, and Cl atoms, and comparison of the vibrational-rotational energy distributions of the products with quasiclassical calculated results led to an understanding of the reaction dynamics.¹¹⁻¹⁴ In recent work¹⁵ we have used the infrared emission technique to analyze the vibrational excitation of isotopic water molecules formed in the reactions of OH(OD) radical with HBr and DBr,

$$OH(OD) + HBr \rightarrow H_2O(HOD) + Br.$$
 (1) and (1D)

Chemiluminescent spectra in the $2400-3900 \text{ cm}^{-1}$ range were recorded by a Fourier transform spectrometer and analyzed using computer simulation. The spectra were obtained from a fast-flow reactor with 0.5-2.0 Torr of Ar for a short reaction time (0.2-0.8 ms). The degree of vibrational coupling among levels was determined, and it was shown that the distributions for $v_1 + v_3$ and v_2 of H₂O and v_3 and $v_1 + v_2$ for HOD could be assigned. The fraction of vibrational energy was 0.61 in H₂O and 0.65 in HOD, and the vibrational distributions showed an inverted population in both the stretching and bending modes, as would be expected for a direct abstraction mechanism. These experimental results can be compared to a quasiclassical trajectory calculation⁸ and a quantum scattering calculation of Clary et al.9 on an approximate potential, which was constructed so as to provide a negative temperature dependence for the rate constant of reaction (1).

In the present work we have studied the reactions of OH(OD) radicals with HI and GeH_4 . Both reactions have larger rate constants than reaction (1) and presumably they

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TABLE I. Thermodynamical and kinetic data for the $OH(OD)+HR \rightarrow H_2O(HOD)+R$ (R=Br, GeH₃, I) reactions.

	$D_0(H-R)^a$	$-\Delta H_0$	E_a^{b}	$\langle E_{\rm av} \rangle$	k (298 K)
Reaction		cal mol	1		cm^3 molecule ⁻¹ s ⁻¹
OH+HBr	86.64±0.05	31.4	0	33.7	1.1×10^{-11} b
OD+HBr		30.8	0	33.1	$k_{\rm H}/k_{\rm D} = 1.3 \pm 0.2^{\rm c}$
OH+HI	70.42 ± 0.06	47.7	0	49.8	2.7×10^{-11} b
OD+HI		47.1	0	49.2	$k_{\rm H}/k_{\rm D} = 1.0 \pm 0.2^{\rm c}$
$OH+GeH_4$	82 ± 2^d	36	^e	38.4	$(7\pm1)\times10^{-11}$ c
$OD + GeH_4$		36		37.8	$k_{\rm H}/k_{\rm D} = 1.4 \pm 0.1^{\rm c}$

^aReference 17(a).

^bReference 1.

^cThis work.

^dSee also Refs. 17(b) and 17(c) for a discussion about Ge–H bond energy. ^e E_a =0 can be assigned with the reference to the E_a =0.095 kcal mol⁻¹ for OH+SiH₄ \rightarrow H₂O+SiH₃ reaction (Ref. 44).

also proceed without formal potential energy barriers. The rate constant for HI is 2.7×10^{-11} molecule cm⁻³, which is 2.5 times larger than for HBr.¹ The chemistry of GeH₄ may be important in the plasma-enhanced chemical vapor deposition processes,¹⁶ but neither dynamical nor kinetic data currently exist for the OH+GeH₄ reaction.

The infrared chemiluminescent spectra of H_2O and HOD were measured from the reactions of OH and OD radicals with HI and GeH₄ in the same reactor that was used for reaction (1),

$$OH(OD)+HI \rightarrow H_2O(HOD)+I$$
, (2) and (2D)

$$OH(OD)+GeH_4 \rightarrow H_2O(HOD)+GeH_3$$
, (3) and (3D)

These reactions were selected because the exoergicity is larger than in the OH+HBr reaction and because both reactants have been studied with O, F, and Cl atoms.^{11–14} The energy available to the products can be obtained from the enthalpy changes for reactions (1)-(3) using Eq. (4),

$$\langle E_{\rm av} \rangle = -\Delta H_0^0 + nRT + E_a \,, \tag{4}$$

where E_a is the activation energy and n=3.5 for reactions (1) and (2) and n=4 for reaction (3). The thermodynamical and kinetic data for these reactions are listed in Table I. One of the interesting features of this group of reactions is the zero activation energy. The reduced rate constants, relative to the collision rate constant, arise as a consequence of the orientation requirements for the OH(X $^{2}\Pi$) radical. The $-\Delta H_{0}$ values, obtained from the H-R bond energies,¹⁷ are 31.4, 47.7, and 36.0 kcal mol^{-1} for the OH reactions. The available energies are sufficient to excite four and three stretching quanta of the water molecule in reactions (2) and (3), respectively. The large rate constants of reactions (2) and (3) made it possible to observe chemiluminescence in the 2200-3900 plus the $4500-5500 \text{ cm}^{-1}$ range; the latter was used to compare emission intensities from the $(\Delta \nu_3 = -1 + \Delta \nu_2 = -1)$ combination transition to the $\Delta \nu_3 = -1$ transition.

The experimental chemiluminescent spectra were analyzed using computer simulation methods previously developed.^{15,18} Some improvements concerning line positions of the combination and hot bands and intensity corrections for centrifugal effects, which were introduced in the present study, are described in Sec. III. The vibrational distributions are presented in Sec. IV B. In spite of the available energy being higher than for OH+HBr, the vibrational distributions from both HI and GeH₄ were noninverted in the stretching mode. Information theoretical analysis, which is given in detail in Sec. V A, showed that the surprisal plots for OH+GeH₄ and OD+GeH₄ reactions are linear, but the slopes are lower than those for the OH+HBr and OD+HBr reactions. The surprisal plots for OH+HI and OD+HI reactions also are linear, but the slopes are close to zero. The detailed discussion of the reaction mechanisms, along with a comparison with results from reactions with F, Cl, and O atoms, is given in Sec. V B.

In addition to providing vibrational distributions, the infrared chemiluminescence can be used to obtain relative rate constants for H_2O and HOD formation by comparison with a standard reaction. In this work the rate constant for the reaction of OH radical with germane was obtained by comparison to HBr. The secondary kinetic-isotope effects for the GeH₄ and HI reactions with OH and OD were obtained by comparison of the H_2O and HOD emission intensities.

II. EXPERIMENTAL METHODS

The experimental methods were given in the preceding paper¹⁵ that described our study of the HBr reaction. The infrared chemiluminescence spectra from vibrationally excited H₂O and HOD molecules generated by the reactions of OH and OD radicals with hydrogen containing molecules were recorded by a Fourier transform infrared spectrometer (BIORAD FTS-60), which observed the emission from a fast-flow chemical reactor operated at 300 K. The spectral resolution was 1 cm⁻¹. The spectrometer chamber and the tube connecting the observation window (NaCl) with the spectrometer inlet lens (CaF₂) were continuously flushed with dry air to remove water vapor that would absorb the chemiluminescent radiation. The response of the liquid N₂ cooled InSb detector was calibrated with a standard blackbody source.

The OH or OD radicals were produced 30 cm upstream of the observation window (NaCl) via the H(D)+NO₂ reaction; the H(D) atoms were generated by a discharge through a H₂(D₂)/Ar mixture. The degree of the dissociation of H₂(D₂) was measured as 50%.¹⁹ Molecular reactants were introduced 3.5 cm upstream of the observation window. Typical concentrations of GeH₄ and HI in the flow reactor were about 2×10^{13} molecule cm⁻³. The total pressure was varied from 0.3 to 1.2 Torr using Ar as the carrier gas. The typical reaction time (at 0.5 Torr) was 0.25 ms.

The secondary reaction of germyl radical

$$OH + GeH_3 \rightarrow H_2O + GeH_2$$
 (5a)

$$\rightarrow$$
 H₂+GeH₂O (5b)

must be considered, because the formation of water in channel (5a) could effect the H_2O spectra from the primary reaction (3). The ratio of water concentrations produced in the secondary and primary steps at short reaction times may be expressed as $[H_2O]_{sec}/[H_2O]_{pri}=k_{5a}[OH]\Delta t/2$. For typical conditions of 0.5 Torr, $[OH]=2\times10^{13}$ molecule cm³ and $\Delta t=0.25$ ms, comparable $[H_2O]_{sec}$ and $[H_2O]_{pri}$ may be achieved only if $k_{5a}>1\times10^{-10}$ cm³ molecule⁻¹ s⁻¹. Moreover, when reaction (3) takes place with an excess of NO₂ over the H atom concentration, reaction (6), with $k_6=(1.06\pm0.18)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Ref. 20) effectively removes the GeH₃ radicals,

$$NO_2 + GeH_3 \rightarrow products.$$
 (6)

A suggested mechanism for reaction (6) is formation of a GeH_3NO_2 complex, followed by isomerization to GeH_3ONO and decomposition to GeH_3O+NO or GeH_2+HONO . The reaction with NO

$$NO+GeH_3 \rightarrow GeH_3NO$$
 (7)

with $k_7 = (1.02 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Ref. 20) is an order of magnitude slower and can be neglected, because [NO₂]>[OH]=[NO]. To examine whether reaction (5a) plays any role in our system, water emission spectra were recorded for [NO₂]=1×10¹⁴ and [GeH₄]=1.6×10¹³ molecule cm⁻³ with OH concentrations of 3.0, 1.2, 0.65, and 0.23×10¹³ molecule cm⁻³. All four spectra were identical, within the experimental error limits, confirming the insignificance of the secondary reaction (5a). For most experiments, we used [OH]≈2×10¹³ molecule cm⁻³ with excess NO₂ in order to have a better signal to noise ratio.

Commercial tank grade Ar was passed through three molecular sieve traps cooled by acetone/dry ice mixture and liquid N₂ to reduce H₂O and CO₂ impurities. The HBr and HI (Matheson) were purified by two freeze–pump–thaw cycles before the gases were loaded into gas storage reservoirs as 10% mixtures with Ar. Tank grade H₂(D₂) and germane (Solkatronic Chemicals Inc.) were used without purification. The GeH₄ was metered to the reactor from a reservoir containing a 10% mixture with Ar. Germane is a highly flammable material and should be handled with caution.

III. SIMULATION METHODS

A. Modeling of H₂O spectra

As in our previous works,^{15,18} computer simulation of the H₂O spectra was used to assign the vibrational distributions. The procedure begins with the relative line intensities for the (001) and (100) fundamental bands as measured in absorption.²¹ The corresponding emission bands were calculated as in Ref. 18(a) with a Boltzmann rotational population. Only the modifications and details necessary for clarity of reading the present paper are given below. Line positions for all the $(v_1, v_2, v_3) \rightarrow (v_1, v_2, v_3 - 1)$ and (v_1, v_2, v_3) $\rightarrow (v_1 - 1, v_2, v_3)$ higher bands involved in the H₂O spectra were obtained as a difference of the rovibrational energy levels of the corresponding transitions. Since the energy available for the OH+HI reaction is sufficient to excite up to four H₂O stretching quanta, the bands with $v_1 + v_3 = 4$, $v_2 \leq 2; v_1 + v_3 = 3, v_2 \leq 4; v_1 + v_3 = 2, v_2 \leq 6; \text{ and } v_1 + v_3 = 1,$ $v_2 \leq 6$ energy levels must be considered. Transitions between the rotational levels with $J \leq 7$ (all K_a , K_c), J = 8 $(K_a - K_c < 2), J = 9 \quad (K_a - K_c < -5) \text{ and } J = 10$ $(K_a - K_c < -6) \text{ are responsible for the bulk of the observed}$ emission intensity.¹ Fortunately, many H₂O bands in the $0-17\ 000\ \mathrm{cm}^{-1}$ spectral range have been thoroughly examined, and most of the rovibrational energy levels for v_1 , $v_3 \leq 4$, $v_2 \leq 2$, and $J \leq 8$ states are known. This includes (010),²² (020), (100), and (001),²³ (030), (110), and (100),²⁴ (040), (101), (120), (021), (200), and (002),^{25–28} (050), (130), (031), (210), (111), and (012),^{29–32} (211), (131), $(310), (112), (013), {}^{32,33}, (041), (220), (121), (022), (300),$ (201), (102), and (003),^{32,34} (141), (320), (221), (301), (202), (122), (023), (400), (103), (004), (231), (212), (311), (410), and (113) (Ref. 35) absorption bands. Missing levels were calculated using expressions for rotational energy from Ref. 26, neglecting J- and K-dependent terms for Fermi and Darling-Dennison interactions. Where possible, rotational constants for vibrational states from Refs. 22-35 were used; other cases were obtained by linear extrapolation of the rotational constants of lower states. The energy levels for states with $v_2=5$ and 6 (with poor convergency for $J \ge 6$) were calculated using a polynomial extrapolation of the rotational levels of $v_2=0, 1, 2, 3$, and 4 states. As a rule, values for band centers were taken from the HITRAN database. Some experimental values for high v_2 states [e.g., (151) and (042)] were taken from Ref. 36, the others were obtained from variational calculations.37,38

The close energy of symmetric and antisymmetric stretching vibration levels leads to fast collisional equilibration between these energy levels, and only the equilibrium population, $v_{1,3}$, can be observed in our experiments. Hence, the simulated spectra for H₂O were calculated as a superposition of the "equilibrated" ($v_{1,3}$, v_2) bands. Omitting terms with a negligible 298 K Boltzmann weight, gives the following ($v_{1,3}v_2$) groups:

$$(1,v_2) = 0.384(0,v_2,1) + 0.616(1,v_2,0), v_2 = 0-6;$$

$$(2,v_2) = 0.15(0,v_2,2) + 0.38(1,v_2,1) + 0.47(2,v_2,0),$$

$$v_2 = 0-6;$$

$$(3,v_2) = 0.054(0,v_2,3) + 0.119(1,v_2,2) + 0.400(2,v_2,1) + 0.427(3,v_2,0), v_2 = 0-4;$$

$$(4,v_2) = 0.043(1,v_2,3) + 0.440(2,v_2,2) + 0.434(3,v_2,1),$$

$$v_2 = 0-2.$$
(8)

The harmonic oscillator approximation with a cubed frequency adjustment³⁹ was used to calculate the intensity of the $\Delta v_3 = -1$ and $\Delta v_1 = -1$ bands from the $(v_{1,3}, v_2)$ states of Eq. (8). In this work, a correction to the line intensities of the $\Delta v_3 = -1$ combination bands was made with the help of *F* factors, which reflect a deviation of the transition intensity from the rigid-rotor approximation.^{40,41} The *F* factors were calculated according to the theory of the first-order intensity perturbations for the vibration-rotation lines of asymmetric rotors developed by Braslawsky and Ben-Aryen for fundamental bands.⁴⁰ The theory was extended to give correction factors for combination and hot bands; the relevant formulas

TABLE II. Band strength coefficients for the equilibrated H₂O and HOD emission bands.

	H ₂ O								HD	0	
	Band	centers	$[\nu_0(i)/\nu_0(1)]^3$		$v_{1,3}[v_0(i)/v_0(2)]^3$				Band	$[v_i(i)]$	
Band	ν_3	ν_1	ν_3	ν_1	ν_3	ν_1	α^{a}	Band	center	$[\nu_0(1)]^3$	α^{a}
$(1, v_2)$	3756	3657	1	1	1	1	0.427	$(v_{1,2},1)$	3707	1	1
$(2, v_2)$	3689	3545	0.947	0.911	1.894	1.822	0.719	$(v_{1,2},2)$	3543	0.873	1.75
$(3, v_2)$	3587	3398	0.871	0.802	2.613	2.406	0.908	$(v_{1,2},3)$	3381	0.759	2.28
(4, <i>v</i> ₂)	3505	3621	0.813	0.971	3.252	3.884	1.576	$(v_{1,2},4)$	3204	0.646	2.58

^aBand strength coefficient, α , is defined as $S_{\nu}^{0}(v_{1}/v_{2}/v_{3}) = \alpha S_{\nu}^{0}(001)$; see text for example.

are presented in the Appendix. The band centers of the $v_{1,3}=1, 2, 3$, and 4 emission spectra are separated by ~90 cm⁻¹, which allows the v_2 distribution of each $v_{1,3}$ level to be assigned with confidence. Selection of a vibrational population to fit a given experimental spectrum was made using a least-squares procedure with normalization of the calculated spectrum to the peak with maximum intensity in the experimental spectrum.

Integrated intensity measurements were employed in the following sections for the evaluation of rate constants. Some equations are given below to explain the relations between the observed intensities from H₂O for different reactions. The absorption band sum intensities²¹ of H₂O are $S_v^0(\nu_3)$ $=7.20\times10^{-18}$ and $S_v^0(\nu_1)=4.96\times10^{-19}$ cm⁻¹/molecule cm^{-2} , giving a ratio of 0.069. Since the frequency difference is not large, we assume the ratio to be valid for the emission bands as well. Using this ratio, Eq. (8), and the corrected harmonic oscillator approximation, we obtained estimates for the band strength coefficients of the equilibrated $\nu_{1,3}$ bands that are presented in Table II. For example, the $(2, v_2)$ emission consists of two $\Delta v_3 = -1$ bands from $(0, v_2, 2)$ and $(1,v_2,1)$ states and two $\Delta v = -1$ bands from $(1,v_2,1)$ and $(2,v_2,0)$ states. The Boltzmann weights are determined by Eq. (8), and vibrational band strength are equal to $1.89S_v^0(\nu_3)$ and $1.00S_v^0(\nu_3)$, respectively, for the two $\Delta v_3 = -1$ bands and $1.00S_v^0(v_1)$ and $1.82S_v^0(v_1)$, respectively, for the two $\Delta v_1 = -1$ bands. Taking into account the $S_v^0(\nu_1)/S_v^0(\nu_3)$ ratio, the resulting emission strength for $(2, v_2)$ is calculated as $0.15[1.89 \cdot S_v^0(\nu_3)] + 0.38[1.0 \cdot S_v^0(\nu_3) + 0.07 \cdot S_v^0(\nu_3)] + 0.47[1.82 \cdot 0.07 \cdot S_v^0(\nu_3)] = 0.72S_v^0(\nu_3)$, as presented in Table II.

B. Modeling of HOD spectra

The spectroscopic database for HOD is much more limited than for H_2O , hence, the positions of the emission bands from high levels were approximated by red-shifting the origins of the fundamental bands, as we described in Ref. 15. The magnitude of the shift was calculated as a difference of band centers, which were taken from the HITRAN database and Ref. 42. Band centers for transitions that were not previously reported were calculated using the conventional expression for the vibrational energy levels with anharmonic and Fermi-resonance constants provided in Ref. 42.

One very important advantage of the HOD spectra, relative to the H₂O spectra, is that emission from the ν_3 mode $(3000-3900 \text{ cm}^{-1})$, which is supposed to be the "active" mode⁸ for the OD reactions under study, is not overlapped with emission from any other normal mode, and the ν_3 levels are not collisionally coupled to any other set of levels. Hence, the nascent ν_3 distribution can be uniquely obtained by examining the $\Delta \nu_3 = -1$ HDO spectra from reactions (2D) and (3D). Furthermore, simulation of the $\Delta \nu_1 = -1$ HOD spectra (2300–3000 cm^{-1} range) gives the population in the $v_3=0$ level, except for the dark (000) and (010) states. However, the latter population can be estimated by either assuming a similarity to the ν_1/ν_2 distribution in the $\nu_3=1$ state or by extrapolation of the ν_2 distribution of the $\nu_3=0$ level. A disadvantage of the HOD molecule is that populations in the ν_1 and ν_2 modes cannot be assigned separately, because the small energy difference between the v_1 and $2v_2$ levels leads to rapid collisional equilibrium within the ν_1 , ν_2 ($\nu_2 \ge 2$) sets of levels. Accordingly, the obtained distributions are defined by the $\nu_{1,2}$ equilibrium state denoted by the equivalent number of bending quanta. For example, the $(4, v_3)$ level is composed of three states; $a_1(0,4,v_3) + a_2(1,2,v_3) + a_3(2,0,v_3)$, where the 300 K Boltzmann weights are $a_1=0.333$, $a_2=0.253$, and $a_3=0.414$ for $v_3=1$; $a_1=0.364$, $a_2=0.260$ and $a_3=0.376$ for $v_3=2$, etc. The band strength coefficients, which are used below to determine the secondary kineticisotope effect for reactions (1D)-(3D), are given in Table II.

IV. RESULTS

A. Experimental chemiluminescent spectra: 2200–3900 cm⁻¹ range

The H₂O emission spectra from reactions (1)–(3) in the range of 2950–3900 cm⁻¹, corrected for the detector response function, are shown in Fig. 1. This range includes the $\Delta \nu_1 = -1$ (symmetric stretch) and $\Delta \nu_3 = -1$ (antisymmetric stretch) bands of H₂O. The spectra were collected at 0.5 Torr and a reaction time of 0.25 ms with [OH] in the range of $(1-2)\times10^{13}$ molecule cm⁻³. Each spectrum represents the average of 512 scans of the spectrometer. The superimposed dotted curves represent the calculated spectra with vibrational distributions to be given in the next section.

The possibility of vibrational relaxation (beyond the coupling of ν_1 and ν_3 of H₂O and ν_1 and ν_2 of HOD) has been discussed earlier.^{15,18} The rate constants from Ref. 43 show that the quenching of H₂O($\nu_{1,3}$ =1) by Ar is not important for ≤ 0.7 Torr and our residence time. Due to the large





FIG. 1. Infrared emission spectra in the 2940–3900 cm⁻¹ range produced by the reactions of OH with HBr, GeH₄ and HI at 0.5 Torr. The spectra, which have been corrected for the detector response function, are plotted with normalization to the maximum peak intensity. (a) OH+HBr reaction with [OH]=1.2, [HBr]=1.6; (b) OH+GeH₄ reaction with [OH]=1.9, $[GeH_4]=1.5$; (c) OH+HI reaction with [OH]=1.7, [HI]=2.5 (the concentrations are in units of 10^{13} molecule cm⁻³). The dashed lines show the best-fit simulated spectra.

signal from reaction (2), we could show that identical H_2O spectra were obtained at 0.34, 0.46, and 0.71 Torr of Ar for $\Delta t = 0.35$ ms with the same reactant flows, confirming the insignificance of quenching by Ar in this pressure range. The distributions from these spectra are shown later in Table IV. Similar conclusions¹⁵ previously were reached about the distributions assigned to reaction (1). Since the $v_{1,3}$ distribution from HBr is inverted, vibrational relaxation would be especially noticeable. Other probable quenching agents are OH radicals, NO, NO₂, and reactant molecules. For each reaction, we tested experimentally the range of reactant concentrations, [RH], for which (i) the integrated spectral intensity was linear vs [HR] and (ii) the relative intensity of the prominent peaks in the spectra remained constant. For a reaction time of 0.35 ms (P=0.7 Torr), these concentrations are $[HBr] = [HI] \approx 2.8 \times 10^{13}$, $[GeH_4] \approx 1.5 \times 10^{13}$ molecule cm^{-3} . Using the OH+HBr reaction as a test case, the range of [OH] was determined that satisfied the same criteria, and the [OH] was $<2.5\times10^{13}$ molecule cm⁻³. No effects of relaxation was observed up to $[NO_2] = 3 \times 10^{14}$ molecule cm⁻³.

The HOD emission spectra from reactions (1D)–(3D) in the range of 2200–3900 cm⁻¹, corrected for the detector response function, are shown in Fig. 2. The spectra were measured at 0.5 Torr for $\Delta t=0.25$ ms, reagent concentrations of about 1×10^{13} molecule cm⁻³ and [OD] of about $(1-2)\times10^{13}$ molecule cm⁻³. The weak emission in the 2200–3000 cm⁻¹ range consists of $\Delta \nu_1=1$ (O–D stretch) and $\Delta \nu_2=-2$ (bend) bands. The strong emission in the

FIG. 2. Infrared emission spectra in the 2200–3900 cm⁻¹ range produced by the reactions of OD with HBr, GeH₄ and HI at 0.5 Torr. The spectra, which have been corrected for the detector response function, are plotted with normalization to the maximum peak intensity. (a) OD+HBr reaction with [OD]=1.9, [HBr]=0.8; (b) OD+GeH₄ reaction with [OD]=1.6, [GeH₄]=1.3; (c) OD+HI reaction with [OD]=1.2, [HI]=1.7 (the concentrations are in units of 10¹³ molecule cm⁻³). The dashed lines represent the best-fit simulated spectra.

3000–3900 cm⁻¹ range consists of $\Delta \nu_3 = -1$ (O–H stretch) bands of HOD. The emission intensity in the 2200-3000 cm⁻¹ range is visibly higher for the HI and GeH₄ reactions than for the HBr reaction. Since the O-D spectator bond in HOD is not expected to be excited in this type of H atom abstraction reaction, this immediately gives evidence for a higher bending excitation and/or a higher population in $v_3=0$ from reactions (2) and (3) compared to reaction (1). The greater intensity from lower wavenumbers in both bands that is clearly evident in Figs. 2(a), 2(b), and 2(c) from the HI and GeH₄ reactions corresponds to an overall increase of vibrational excitation from reactions (2) and (3), relative to the HBr reactions. The HOD spectra demonstrate more distinct differences among the three reactions than the H₂O spectra, because excitation in the new H₂O bond leads to both ν_3 and ν_1 excitation and, furthermore, these levels are collisionally mixed in H₂O. The detailed vibrational distributions derived from these spectra are presented in the next section.

B. Vibrational distributions for H₂O and HOD

The best simulated H₂O and HOD spectra for the 0.5 Torr data are shown in Figs. 1 and 2 by the dotted curves and the corresponding distributions are presented in Tables III and IV. Only populations in the $v_{1,3} \ge 1$ and v_2 levels can be obtained from simulation of the H₂O spectra. The total population in a given $v_{1,3}$ level, $P_{1,3}$, was obtained by summation over the specific v_2 populations. The $P_{1,3}$ values are pre-

TABLE III. Vibrational distributions of H_2O from reactions (1), (2), and (3).

				v_2							
v _{1,3}	0	1	2	3	4	5	≥6	$P_{1,3}{}^{a}$	$P_{1,3}{}^{b}$	$P_{1,3}{}^{c}$	$P_{1,3}^{st}$
					OH-	-HBr					
0									22	14	53.1
1	8.9	13.2	10.4	8.4	4.5	3.5		48.9	38	42	35.5
2	16.9	17.7	3.9	2.9				41.4	32	36	10.9
3	6.5	3.1						9.6	7.5	8	0.5
$P_2^{b,d}$	30.4	33.1	15.4	12.1	5.2	4.0	•••				
$P_2^{\rm st}$	41.4	26.2	15.8	8.9	4.6	2.1	1.0				
					ОН	+HI					
0					•••			•••	54	42	35.3
1	11.7	11.3	11.7	12.2	6.9	2.8	1.6	58.3	27	34	34.2
2	11.1	8.3	2.0	3.2	0.6	0.2		25.4	12	15	20.6
3	4.4	4.4	3.9	2.1				14.8	7	9	8.3
4	1.2	0.4						1.4	0.6	0.8	1.7
$P_2^{b,d}$	24.9	22.3	18.7	18.9	9.3	3.9	2.0				
$P_2^{\rm st}$	31.9	22.9	16.2	11.1	7.2	4.6	5.9				
					OH+	GeH4	•				
0					•••				44	33	47.0
1	11.5	13.6	12.7	14.6	4.4	2.8	0.7	60.2	34	40	36.0
2	10.7	9.6	4.1	4.1				31.4	17	21	14.6
3	6.3	4.8						8.4	5	6	2.3
$P_2^{b,d}$	24.5	25.7	18.5	21.0	5.7	3.6	0.9				
P_2^{st}	38.5	25.0	16.0	9.8	5.6	3.0	2.2				

^aPopulation in $v_{1,3}=0$ is not considered.

^bPopulation in $v_{1,3}=0$ is assumed to be equal to the population in $v_3=0$ for the similar reaction with OD.

 $^{c}P_{1,3}(0)$ from linear surprisal plots (model I prior).

^dBending distribution in $v_{1,3}=0$ is assumed to be the same as in $v_{1,3}=1$. ^eStatistical distributions calculated for model I prior.

sented in the last four columns of Table III, normalized to 100% for different assignments of the $P_{1,3}(0)$ population; (a) $P_{1,3}(0)$ was not considered; (b) $P_{1,3}(0)$ was assumed to be similar to the $P_3(0)$ that was experimentally determined from the HOD distributions; (c) $P_{1,3}(0)$ was obtained from linear surprisal plots. These experimental distributions are compared to the calculated statistical distribution, P_3^{st} . Although the vibrational distributions for reaction (1) were deduced from new data, they are the same as given in Ref. 15 and they are included here for convenient reference. The experimental distributions decline with increasing $v_{1,3}$ for both reactions (2) and (3), but the range of v_2 extends to the thermochemical limit for each $v_{1,3}$ level. The OH+HI reaction has a more extended stretching distribution in agreement with larger available energy, but the population of the ground stretching state exceeds that from the GeH₄ reaction, according to both (b) and (c) assignments of $P_{1,3}(0)$. It is also noteworthy that the population in the highest $v_{1,3}=3$ level from reaction (3), which is within 0.79 of the energy limit, is significantly higher than the population in $v_{1,3}=4$ from reaction (2), which has an energy equal to 0.7 of the thermochemical limit. The maximum population for both reactions is in the $v_{1,3}=1$, $v_2=3$ state. The global H₂O bending distribution, P_2 , was obtained by summation over all $v_{1,3}$ states with a certain v_2 number; these are given in the bottom line of each distribution in Table III. The rather abrupt decrease in the $v_2=4$ population that seems to exist for all three reactions probably is a defect of the simulation procedure.

Table IV presents the H₂O vibrational distributions derived from the spectra of reaction (3) obtained at Ar pressures of 0.34, 0.48, 0.70, 1.0, and 1.2 Torr. These spectra were analyzed in order to identify the onset of vibrational relaxation. To within the reliability of the assignment of the distributions, the stretching populations, $P_{1,3}$, do not change with pressure in the 0.34–0.70 Torr range. A gradual growth of the population in the $v_{1,3}=1$ level is evident from the spectra at 1.0 and 1.2 Torr. These distributions confirm that vibrational relaxation by Ar is insignificant at ≤ 0.7 Torr and $\Delta t \leq 0.35$ ms.

The vibrational distribution given in Table V for the OD +HBr reaction is the same as presented in Ref. 15. This distribution, which serves as the reference for direct abstraction, was confirmed again from new spectra obtained in the present work. The HOD(v_3) distributions for reactions (2) and (3) in Table V are similar to the H₂O($v_{1,3}$) distributions in that they extend to the thermodynamic limits and decrease with increase of v_3 . The populations in $v_3=0$ states were

TABLE IV. Vibrational distributions of H_2O from modeling the chemiluminescence spectra from $OH+GeH_4$ at different reactor pressures.^a

P				v	2				
(Torr)	v _{1,3}	0	1	2	3	4	5	≥6	$P_{1,3}$
0.34	1	11.4	13.7	12.5	14.5	4.2	1.0	2.8	60.1
	2	11.0	10.3	4.0	4.5				29.8
	3	5.3	4.4	0.4					10.1
	P_2	27.7	28.4	16.9	19.0	4.2	1.0	2.8	
0.46	1	11.4	13.0	13.8	13.5	4.7	1.1	2.5	60.0
	2	11.1	9.5	4.4	5.0				30.0
	3	4.4	4.8	0.8					10.0
	P_2	26.9	27.3	19.0	18.5	4.7	1.1	2.5	
0.71	1	13.3	11.5	11.0	11.1	6.3	3.4	4.9	61.5
	2	12.2	7.5	2.8	6.5				29.0
	3	3.2	5.9	1.2					10.3
	P_2	29.0	24.9	15.0	17.6	6.3	3.4	4.9	
1.0	1	16.9	16.0	12.6	11.5	2.3	2.8	3.1	65.0
	2	11.5	8.4	2.3	3.7				25.9
	3	3.1	4.6	1.4					9.0
	P_2	31.5	29.0	16.3	15.2	2.3	2.8	3.1	
1.2	1	20.8	20.3	15.9	12.0	1.8			70.8
	2	8.9	6.3	4.7	1.5				21.4
	3	2.9	3.9	1.0					7.8
	P_2	32.6	30.5	21.6	13.5	1.8			

^aPopulation in $v_{1,3}=0$ is not considered.

TABLE V. Vibrational distributions of HDO from reactions (1D), (2D), and (3D).

					v_2							
<i>v</i> ₃	0	1	2	3	4	5	6	7	≥8	P_3^{a}	P_3^{b}	$P_3^{\rm st}$
					0	D+HBr						
0	2.6 ^c	2.3 ^c	3.7	6.1	2.0	3.5	0.9	0.3		21.7	21.7	76.2
1	6.7	5.9	6.3	4.9	4.1	2.6	1.7	0.8		33.0	33.0	20.5
2	12.5	9.7	7.1	4.9	2.3	0.8				37.3	37.3	3.2
3	2.9	2.8	0.1							5.8	5.8	0.1
$P_{1,2}^{a}$	24.7	20.7	17.2	15.9	8.4	6.9	2.6	1.1				
$P_{1,2}^{st}$	22.3	15.8	21.4	13.7	12.9	7.0	4.7	1.8	0.4			
					C	DD+HI						
0	6.1 ^c	5.0 ^c	8.2	4.8	4.6	6.0	5.1	4.4	9.6	53.8	59	62.9
1	4.2	3.9	3.5	1.8	4.4	6.5	3.2	0.7		28.2	25	25.8
2	3.1	3.9	1.0	3.4	2.5	3.0				16.9	15	8.9
3	0.6	0.6	0.4							1.6	1.4	2.2
4	0.4	0.1								0.5	0.4	0.3
$P_{1,2}^{a}$	14.4	13.5	13.1	10.0	11.5	15.5	8.3	5.1	9.6			
$P_{1,2}^{st}$	13.1	10.3	15.8	11.9	13.4	9.6	9.1	6.0	10.8			
					OE	0+GeH₄ ^d						
0	6.9 ^c	5.3°	8.4	8.5	4.4	5.5	2.6	1.4	1.2	44.2	41	72.0
1	5.7	5.2	6.2	2.8	1.1	2.2	3.1	2.8		29.1	31	22.7
2	6.9	5.3	2.8	2.1	3.4	2.6				23.1	24	4.9
3	1.9	1.8								3.7	4	0.5
P_{12}^{a}	21.4	17.6	17.4	13.4	8.9	10.3	5.7	4.2	1.2			
$P_{1,2}^{st}$	18.9	13.7	19.7	13.6	13.5	8.4	6.5	3.3	2.4			

 ${}^{a}P_{3}(0)$ from the simulation.

 ${}^{b}P_{3}(0)$ from the linear surprisal plots (model I prior).

^cPopulation in dark (000) and (010) states obtained using the analogy to the populations in (000), (010), and (020) for statistical distribution (model I prior).

 ${}^{d}P_{3}^{st}$ and $P_{1,2}^{st}$ are the statistical distributions calculated for model I prior.

obtained from modelling the $\Delta v_1 = -1$ plus $\Delta v_2 = -2$ emission, as shown in Fig. 2. Estimation of the population in (000) and (010) states was made by analogy with the relative population of (000), (010), and (020)/(100) states in the statistical distribution. The statistical calculation gives 6.4, 5.3, and 4.3+4.3 as the relative populations for the (000), (010), and (020)+(100) levels, respectively, for the HI reaction and 11.0, 8.5, and 6.6+6.6 for the GeH₄ reactions. After knowing the population in (020)+(100) level, the populations in the (000) and (010) levels were estimated as 0.74 and 0.61 of this value for HI, and 0.83 and 0.64 for GeH₄ reactions. This gave a total of 53.8% and 44.2% for the population in $v_3=0$ for reactions (2D) and (3D), respectively. The contrast between the inverted P_3 distribution from the OD+HBr reaction and the declining distributions from HI and GeH₄ should be noted. Since they were obtained using exactly the same methods, the difference should be reliable. The total populations in a given $v_{1,2}$ state, which were obtained by summation over the v_3 number, are given in the bottom row as $P_{1,2}$. The populations in the $v_{1,2}$ levels extend to the energy limit and the distributions are fairly close to the statistical populations.

C. Rate constant for the OH+GeH₄ reaction

The rate constant of reaction (3) was determined relative to the rate constant of reaction (1) by measuring the inte-

grated H₂O emission intensity from both reactions for constant [OH]. Comparison of the integrated total intensities in the 3000–3900 cm⁻¹ region was made for a range of reactant concentration less than 3×10^{13} molecule cm⁻³. Below this reagent concentration, a linear dependence of the intensity of the H₂O chemiluminescence on reagent concentration was observed, as expected for a reaction following the second-order differential rate law with constant [OH]. Furthermore, the shape of the spectra was unchanged, which insured that the vibrational distributions were constant. Figure 3 shows the dependencies of the H₂O emission intensities from the OH+HBr and OH+GeH₄ reactions measured at 0.7 Torr. On average, the H_2O emission from GeH_4 was 5.8 times stronger than that from HBr. The observed ratio should be corrected to account for the populations of the nonemitting $v_{1,3}=0$ level, which is 21% for HBr and 33% for GeH₄, and for the distributions among the $v_{1,3}=1$, 2 and 3 states. From the distributions, incorporating band strength coefficients from Table II, it follows that the intensity of the normalized spectrum corresponds to $0.38S_n^0(\nu_3)$ and $0.44S_n^0(\nu_3)$ for H₂O from GeH₄ and HBr, respectively. Accordingly, the ratio of the rate constants is $k_3/k_1 = 6.5 \pm 0.9$. Taking $k_1 = 1.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, which is the recommended value,¹ we obtain $k_3 = (7.1 \pm 1.7) \times 10^{-11}$ cm³ molecule $^{-1}$ s $^{-1}$. The lower error limit corresponds to the standard deviations of the slopes in Fig. 3; the upper one includes the uncertainty in the $P_{1,3}(0)$ for reaction (3) (Table III). The GeH₄ reaction appears to be one of the fastest known reaction of hydroxyl radicals with a stable molecule. The value for k_3 agrees with the expected trend in rate constants^{1,44} for OH+CH₄, $k=(7.0\pm0.2)\times10^{-15}$ and OH+SiH₄, $k=(1.2\pm0.2)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹, reflecting the weakening of the H bond. A similar trend of reactivity is observed for oxygen atoms; $k=5.0\times10^{-18}$, 4.8×10^{-13} , and $k=3.2\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ for O+CH₄,⁴⁵ SiH₄,⁴⁵ and GeH₄ (Ref. 46) reactions, respectively.

Reactions of both OH (or OD) and H atoms with GeH₄ also gave a relatively weak emission in the 1900–2200 cm⁻¹ range (see Fig. 4) with a maximum intensity at ~2110 cm⁻¹. This intensity attained 10% of the peak intensity of the H₂O or HOD emission for high flows of GeH₄. This peak matches the *Q*-branch of the ν_3 fundamental vibration (degenerate Ge–H stretch, 2114 cm⁻¹) of the GeH₄ molecule, as concluded from comparison to the vibration-rotation absorption spectrum.⁴⁷ The frequencies of the GeH₃ radical lie in a different range [ν_1 =1839, ν_2 =928, ν_3 =1813, ν_4 =850 (Ref. 48)] We suggest that the observed emission is a result of the nearly resonant *V*–*V* energy exchange process,

$$H_2O(\nu_{1,3}) + GeH_4 \rightarrow H_2O(\nu_2) + GeH_4(\nu_3) \pm 50 \text{ cm}^{-1}.$$
 (9)

The $\nu_3(\text{GeH}_4)$ band strength in absorption,⁴⁹ $\Gamma = 14\,300\,\text{cm}^2\,\text{mol}^{-1}$, converted to the cgs esu system used in the HI-TRAN, is equal to $S_{\nu}^0[\nu_3(\text{GeH}_4)] \approx \Gamma \nu_0/A = 5.17 \times 10^{-17}\,\text{cm}^{-1}/\text{molecule cm}^2$, where $\nu_0 = 2113.6\,\text{cm}^{-1}$, $A = 6.03 \times 10^{23}\,\text{molecule mol}^{-1}$. This S_{ν}^0 value is 7.2 times larger than the ν_3 band sum intensity of H₂O, $7.2 \times 10^{-18}\,\text{cm}^{-1}/\text{molecule cm}^{-2}$. Taking into account the frequency difference $[\nu_3(\text{GeH}_4) = 2110\,\text{cm}^{-1}$ and $\nu_3(\text{H}_2\text{O}) = 3756\,\text{cm}^{-1}]$, the sum intensity ratio for emission becomes equal to ~1.4. At 0.5 Torr, $\Delta t = 0.25\,\text{ms}$ and $[\text{GeH}_4] = 1.5 \times 10^{12}\,\text{molecule cm}^{-3}$, the measured GeH_4^* to H_2O^* integrated intensity ratio is approximately 7×10^{-3} , giving $[\text{GeH}_4^*]/[\text{H}_2\text{O}^*] \approx 0.01$. For these experimental conditions, about 1% of the water molecules were deactivated by reaction (9), which corresponds to a rate constant of the order of $k_9 \sim 3 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.

D. Secondary kinetic-isotope effects

The secondary kinetic-isotope effect for reactions (1)– (3), i.e., the ratio of rate constants for the OH+HR \rightarrow H₂O+R and OD+HR \rightarrow HOD+R reactions, was estimated using the same procedure as used in the previous section for the estimation of the rate constant of reaction (3). The integrated emission intensities of H₂O and HOD in the 3000–3900 cm⁻¹ range were measured in the same experiment with exchange of equivalent H₂ and D₂ flows with the same excess [NO₂]. The average ratio of H₂O to HOD intensity was $I_{H_2O}/I_{HOD} = 0.48 \pm 0.06$ for HBr, 0.49±0.10 for HI, and 0.52 ±0.04 for GeH₄ in experiments at 0.7 (HBr) and 0.5 (HI and GeH₄) Torr. The error limits are the standard deviations for three (HBr and HI) and five (GeH₄) measurements with different reactant concentrations. Using the intensity relations between the equilibrated emission bands from Table II, the

FIG. 3. Dependence of the integrated H₂O emission intensity from the OH+GeH₄ and HBr reactions on reactant concentration for P=0.7 Torr, $\Delta t=0.35$ ms, and [OH]= 2.9×10^{13} molecule cm⁻³.

vibrational stretching distributions from Tables III and V, and taking into account the correspondence between the sum intensities of the v_3 fundamental bands of H₂O and HOD, we obtain $k_{OH}/k_{OD}=1.3\pm0.2$, 1.0 ± 0.2 , and 1.4 ± 0.1 for the reactions with HBr, HI, and GeH₄, respectively. The other directly relevant secondary kinetic-isotope effect available for comparison is $k_{OH}/k_{OD}=1.55\pm0.15$ for the reactions with HCl,⁶ which is close to our value for HBr. The secondary kinetic-isotope effects are generally negligible for other H atom abstraction reactions by OH/OD radicals [for example, the CH₃OOH (1.02±0.10) (Ref. 50) and *n*-butane (0.97 ±0.12) (Ref. 51) reactions].

FIG. 4. Infrared chemiluminescence in the 1900–2100 cm⁻¹ range from GeH₄. (a) OH+GeH₄ reaction for the same conditions as for Fig. 1(b) and $[NO_2]=6.0$; (b) H+GeH₄ reaction with [H]=3.0, $[GeH_4]=1.1$ (the concentrations are in units of 10^{13} molecule cm⁻³).

2000

Wavenumbers (cm⁻¹)

2050

2100

(a)

Emission Intensity

1900

OH+GeH

H+GeH

1950





FIG. 5. Infrared chemiluminescence in the $4500-5500 \text{ cm}^{-1}$ range from combination and overtone emission from the OH and OD reactions with GeH₄ and HI. The experimental conditions are the same as for the experiments described in Figs. 1 and 2.

E. Experimental chemiluminescent spectra: 4500–5500 cm⁻¹ range

Figure 5 shows the H₂O and HOD emission from reaction (2) in the $4500-5500 \text{ cm}^{-1}$ range, arising from the combined $\Delta v_3 = -1 + \Delta v_2 = -1$ transition; this emission was detectable from all three reactions. These spectra can be used to check the intensity relations between the combination and fundamental bands and to confirm the vibrational distributions in Tables III and V. The HITRAN database gives values of $S_v^0 = 7.20 \times 10^{-18}$ and 8.04×10^{-19} cm⁻¹/molecule cm⁻² for H₂O and $S_v^0 = 1.42 \times 10^{-21}$ and 3.67×10^{-23} $cm^{-1}/molecule$ cm^{-2} for HOD for the intensities of the (001) and (011) absorption bands, respectively.²¹ The ratio of the emission intensities, which are proportional to the cube of the transition frequency, can be estimated using the band center frequencies, 3756 and 5331 cm⁻¹ for H₂O and 3707 and 5090 cm^{-1} for HOD, respectively, which gives $S_v^0(\nu_2 + \nu_3)/S_v^0(\nu_3) = 0.32$ for H₂O and 0.067 for HOD. The $4500-5500 \text{ cm}^{-1}$ range also includes (110)–(000) emission from H₂O (ν_0 =5235 cm⁻¹) and (200)–(000) emission from HOD $(\nu_0 = 5372 \text{ cm}^{-1})$. The absorption band sum intensity the former transition is only 3.72×10^{-20} for cm⁻¹/molecule cm⁻²(Ref. 21) and can be neglected. However, the first overtone transitions of ν_1 from HOD are not negligible, $S_v^0 = 1.59 \times 10^{-23}$ cm⁻¹/molecule cm⁻², and they were taken into consideration.

Let us at first consider the emission spectra from the HI reactions, which are shown in Fig. 5. The average ratio of the integrated intensities of the antisymmetric stretch emission, I_3 , and combined antisymmetric stretch+bend emission, I_{23} , obtained from five spectra are $I_3/I_{23}=1.75\pm0.45$ for H₂O

and 2.07 ± 0.09 for HOD. As has been already determined, the sum intensity of the $\Delta \nu_3 = -1$ spectra from HI are equal to $0.42 S_v^0(\nu_3)$ for H₂O and $0.67 S_v^0(\nu_3)$ for HOD. For the same distributions, the calculated sum intensity in the 4500– 5500 cm^{-1} range is equal to $0.74 S_v^0(\nu_2 + \nu_3)$ for H₂O and to $1.02 S_v^0(\nu_2 + \nu_3)$ and $0.17 S_v^0(2\nu_1)$ for HOD. In this calculation, the intensity of the combined emission for the bands with $\nu_2 > 1$ and $\nu_3 > 1$ was assumed to follow the frequency corrected harmonic approximation for the ν_3 mode and the simple harmonic coefficients x_{22} are relatively small for both H₂O and HOD. The calculated ratios of intensities are $I_3/I_{23}=1.7\pm0.3$ for H₂O and 9.0 ± 1.3 for HOD; the agreement is very good with the measured value for H₂O, but the HOD value is 4.3 times larger than the experimental result.

Analogous calculations for the GeH₄ spectra gave sum intensities of 0.59 $S_{v}^{0}(\nu_{2}+\nu_{3})$ for H₂O and 0.99 $S_{v}^{0}(\nu_{2}+\nu_{3})$ and 0.15 $S_v^0(2\nu_1)$ for HOD spectra in the 4500–5500 cm⁻¹ range, and ratios of $I_3/I_{23}=2.0\pm0.3$ for H₂O and 11.4±2.3 for HOD. The measured ratios are $I_3/I_{23}=2.0\pm0.1$ for H₂O and 3.0 ± 0.3 for HOD. In this case the agreement also is excellent between the observed and calculated intensity ratio for H₂O, but the calculated ratio exceeds the experimental value by a factor of 3.8. The most likely reason for the discrepancy with HOD is that the sum intensity $S_v^0(\nu_2 + \nu_3) = 3.67 \times 10^{-23} \text{ cm}^{-1}/\text{molecule cm}^{-2}$ for HOD is underestimated, and the real value is about 4 times larger. It seems possible, since the above value was obtained from only 576 lines identified in the band, while the (001) band of HOD, and (001) and (011) bands of H₂O contain 1651, 1546, and 1306 lines, respectively.²¹

Simulation of the H_2O spectra from reactions (2) and (3) in the 4500–5500 cm⁻¹ range was made in a simplified manner by red shifting the (011)-(000) band, which was calculated from the HITRAN absorption band, to the band centers for transition from higher energy levels. The calculated H₂O (011)-(000) emission band is given in Fig. 5(a) for reference. Using the distribution from Table III for the OH+HI reaction, we obtained the spectrum shown as the dotted curve in Fig. 5(b). For simulation of the HOD spectrum in this range, the (011)-(000) and (200)-(000) HITRAN absorption bands were used in a similar way [see Fig. 5(c)]. The calculated spectrum for the OD+HI reaction using the distribution from Table V is shown in Fig. 5(d). The contribution of the ν_1 overtone emission intensity in this spectra is about 6%. Although the model spectra do not reproduce all the individual strong peaks, they fit the general intensity pattern in a satisfactory way and confirm the vibrational distributions given in Tables III and V.

V. DISCUSSION

A. Reaction mechanisms

Reactions of OH($X^2\Pi$) radicals with HBr and HI proceed to give a single product, H₂O, without a potential energy barrier.¹ However, complications exist in the entrance channel since ${}^{2}A'$ and ${}^{2}A''$ components of the potential surface correlate to OH($X^{2}\Pi$). A similar complication exists on

the product side, since Br or I atoms can be formed in the ${}^{2}P_{1/2}$ state, as well as the ground state. The lower energy ${}^{2}A'$ potential correlates to the ground state product. The possibility of formation of $Br^{*}({}^{2}P_{1/2})$ atoms was discussed before,¹⁵ and it was concluded to be unimportant. A search for $I({}^{2}P_{1/2} \rightarrow {}^{2}P_{3/2})$ emission was made in the HI experiments. A single weak peak was detected in the vicinity of 7600 cm^{-1} from reactions (2) and (2D). The peak height correlated with the intensity of the H₂O and HOD emission and, hence, could be attributed to emission from the $I({}^{2}P_{1/2} \rightarrow {}^{2}P_{3/2})$ transition with $\Delta E = 21.7$ kcal mol⁻¹. The radiative transition probability for this transition is 4.1 times weaker than the $S_v^0(\nu_3)$ of HOD.⁵² The measured intensity ratio for the I* and HOD* emission was of the order of $(3-8) \times 10^{-4}$ from which an upper limit of 0.03% may be set for the formation of I* relative to the ground state iodine atoms. Evidently, formation of the $I^*({}^2P_{1/2})$, either in the primary reaction or as a result of V-E energy transfer, can be neglected for reactions (2) and (2D). We conclude that reaction occurs on the ${}^{2}A'$ potential.

A zero activation barrier for the reaction of OH with GeH₄ is implied by the large rate constant for H₂O formation and from comparison with the $OH+CH_4$ (Ref. 1) and SiH_4 (Ref. 44) family of reactions with $E_a = 3.8$ kcal mol⁻¹ and 0.095 kcal mol⁻¹, respectively. In addition to H abstraction, other product channels for the OH+germane primary reaction could be GeH_3OH+H (substitution) and GeH_3O+H_2 (addition/H₂ elimination). Since enthalpy of formation and bond energy data are available for only a few germanium compounds, we estimated the H₃Ge-OH bond energy from the reaction enthalpy of H₂GeO \rightarrow H₂Ge+O(³P), which is 108 kcal mol^{-1.53} This bond is intermediate between π and semipolar bonding, and the two limiting estimates for the bond strength are $D_0(H_3Ge-OH) \approx 77$ and 54 kcal mol⁻¹. The former is the difference of Ge=O bond strength and a value of 31 kcal mol⁻¹ for the π -bond energy in $H_2Ge=CH_2$ ⁵³ the latter is half of the Ge:O bond energy. Both estimations give positive reaction enthalpies, $\Delta H_0 \approx (5-28)$ and $\approx (3-26)$ kcal mol⁻¹ for the substitution and addition/H₂ elimination channels, respectively. Even being in error by several kcal mol^{-1} , the thermochemistry rules out alternative reaction pathways. However, two microscopic channels for H₂O formation in reaction (3), direct abstraction and addition-migration, may exist.

The rate constants (per H atom) increase in the HBr, GeH₄, HI series and they are 1.1, 1.8, and 2.7×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively. This trend resembles the increase of reaction cross sections with the weight of halogen^{54,55} for the OH+X₂(X=F, Cl, Br, I) series of reactions. This was explained by the decrease of the ionization potential from F₂ to I₂, and the subsequent ability of the halogen molecule to form a radical-halogen bond.⁵⁴ The 300 K rate constant for the direct abstraction OH+HBr reaction has been matched by quasiclassical⁸ and quantum scattering⁹ calculations with Clary's potential. A negative temperature dependence of the OH+HBr reaction was found in ultra-low temperature experiments between 23 and 295 K.¹⁰ A partial explanation is provided by the reduced reaction probability for excited rotational states of OH.^{8,9} This quantum calculation predicted a $B^{1/2}$ dependence of the rate constant, where *B* is the rotational constant of the OH molecule. Substituting the B values of OH for OD gives a factor of 1.4 decrease of the reaction rate in agreement with $k_{OH}/k_{OD} = 1.3 \pm 0.2$ found in the present work for reactions (1)/(1D). A lowering of the OH reaction probability with rotational excitation also was obtained by Nyman and Clary for the $OH+CH_4 \rightarrow H_2O+CH_3$ reaction using the rotating bond approximation,56 and the isotope effect of $k_{OH}/k_{OD} = 1.4 \pm 0.1$ for GeH₄ may be associated with a dependence of the reaction probability on rotational state. On the other hand, the quasiclassical calculations⁸ for OH(OD) with HBr did not give a consistent isotope effect and the variational transition-state theory calculations give a small inverse secondary kinetic-isotope effect. So, the origin of the secondary kinetic-isotope effect is uncertain. The quantum and quasiclassical calculations for potentials of the LEPS type give inverted H₂O and HOD vibrational distributions for reaction (1). The extensive quasiclassical trajectory study⁸ of the OH(OD)+HBr reaction showed that the traditional viewpoint for H-L-H dynamics for triatomic systems was applicable to the vibrational energy disposal to H₂O (HOD), providing that new dynamical aspects associated with excitation of the bending mode (ν_2) were added. The HI and GeH₄ reactions initially were chosen for study because we expected to display direct abstraction dynamics for reactions with larger exoergicity. However, the reactions of OH radical with HI and GeH₄ give vibrational distributions that decline with increasing energy in both the stretch and the bend modes, indicating reaction dynamics that differ from reaction (1). This conclusion rests heavily upon our ability to assign populations in the $v_3=0$ and $v_{1,3}=0$ levels. Since reactions (2) and (3) have been directly compared to reaction (1), this conclusion seems valid. Therefore, the reaction mechanism for HI and GeH₄ must be more complex than direct abstraction with H-L-H dynamics on a LEPS type potential surface.⁴ The surprisal analysis presented in the next section gives a more quantitative measure of the difference between the energy disposal for HBr vs HI and GeH₄ reactions.

B. Surprisal analysis of H₂O and HOD vibrational distributions

The information-theoretical approach to analysis of the H_2O and HOD vibrational distributions was described in our previous report of the OH(OD)+HBr(DBr) reactions.¹⁵ The priors for reactions (2), (2D) are the same as (1), (1D). However, the OH(OD)+GeH₄ reaction needs a different formulation for calculation of the prior vibrational distributions, since the other reaction product is a polyatomic radical, which can accumulate energy in its internal degrees of freedom. Three models were used in which GeH₃ was treated as an atom (I), a rotating symmetric top (II), and a symmetric top with 6 vibrations (III) grouped as follows: 2110(3), 931, 819(2) for calculation of the prior distribution.

The surprisal plot for the experimental HOD stretch distribution from OD+HI is presented in Fig. 6(a). The variable



FIG. 6. Surprisal plots for vibrational stretching distributions (a) HOD from the OD+GeH₄ and HI reactions; (b) H_2O from the OH+GeH₄ and HI reactions.

is the fraction of the available energy in a certain O-H stretching level of HOD, so that $f_{v3}=1$ corresponds to the thermochemical limit. The surprisal for reaction (2D) has a very small slope, $\lambda_{\nu,3} \approx 0$, although the points are scattered. The population in $v_3=0$ of 0.59 obtained from the zero slope surprisal actually agrees with the $P_3=0.54$ value from the spectral simulation. The surprisal parameter for reaction (2D) is very different from reaction (1D), which is also linear but with $\lambda_{n3} = -6.1$. The analogous surprisal plot for OH+HI reaction is shown in Fig. 6(b); the variable $f_{v1,3}$ denotes the fraction of the reaction available energy in a given $v_{1,3} = v_1 + v_3$ state. The surprisal plot for H₂O (P_{1,3}) from HI may be considered as linear with a slope close to zero, although the best fit corresponds to $\lambda_{v1,3}=0.9$. The plus sign of the surprisal slope means that the higher vibrational states have a smaller population than the prior distribution. The $\lambda_{v1,3}$ value, which is a global measure of the energy release to $v_{1,3}$ levels, may be compared with $\lambda_{v1,3} = -4.5$ for the OH+HBr reaction and the surprisal analysis identifies a difference in the dynamics of these reactions. The $P_2(v_2)$ distribution of H₂O given in Table III can be compared to $P_2^{s_1}(v_2)$. A very slight overpopulation in the $v_2=2-4$ levels seems to exist, relative to the statistical limit. The overall $\langle f_v \rangle$ value for the HI reaction is 0.41 (HOD) and 0.36 (H₂O) vs 0.65 (HOD) and 0.61 (H₂O) for the HBr reaction. The energy disposal pattern clearly shows that the dynamics for the HBr and HI reactions are quite different. The most likely explanation is that the OH radical initially attacks the I atom end of H'I, then the H' atom migrates to the oxygen atom and H₂O is ejected; the HI reaction is not a direct process in contradistinction to the HBr reaction.

The three plots for GeH_4 in Figs. 6(a) and 6(b) correspond to different models of the prior for GeH₃ (circles, I; upward triangles, II; and downward triangles, III). The surprisal plots for HOD (P_{v3}) are remarkably linear with slopes $\lambda_{v3} = -3.5, -5.4, \text{ and } -10.8, \text{ respectively. The renormalized}$ $v_3=0$ populations, obtained from the intersection of these linear plots with the ordinate, are 0.41, 0.34, and 0.24, respectively. The former value agrees with the measured population, ~44%, while models II and III seem to give values that are too low. This suggests that GeH₃does not participate in the dynamics or, at least, does not receive much internal energy. The slopes of the surprisal plots for $H_2O(P_{1,3})$ are $\lambda_{v1,3} = -1.5$ (model I), -3.7 (model II), and -9.8 (model III), and the corresponding renormalized populations of the $v_{1,3}=0$ state are 0.33, 0.25, and 0.15. As for HOD, the closest value to the $P_{13}(v_{13}=0)=0.44$ population selected in Table III for H₂O is obtained from model I as a prior.

Let us consider more deeply the assignment of $P_{1,3}(0)$ in reactions producing H₂O. The initial release of energy is to the local mode of the new bond and the old O-H bond is mainly expected to play a spectator role. Since a local H₂O stretch mode is an equal mixture of symmetric and antisymmetric normal modes, the $P_3(0)$ population observed for the O–H mode of HOD also corresponds to the $P_{1,3}(0)$ for H₂O. If the old O-H bond is a perfect spectator with a local distribution of 100% in v = 0, the whole $P_{1,3}$ distribution would coincide with the P_3 distribution of HOD. If, on the other hand, the old bond receives some energy, the resulting $P_{1,3}$ distribution can be obtained as a product of two local distributions. In this case, the statistics for v_3 and $v_{1,3}$ are different, and $P_{1,3}(0)$ is only the fraction of $P_3(0)$ that corresponds to $P_1(0)$. Suppose that the old bond receives a statistical fraction of the reaction energy. For the OH+HBr reaction with $E_{av}=33.5$ kcal mol⁻¹, the statistical probability $P_{\text{local}}^{\text{old}}(0) = 0.74$ and, if $P_{\text{local}}^{\text{new}}(0) = P_3(\text{HOD}) = 0.22$, the combined $P_{1,3}(0)=0.16$. This is very close to the $P_{1,3}(0)=0.14$ value obtained from the surprisal plot.

For the OH+HI reaction with E_{av} =49.8 kcal mol⁻¹, we have $P_{local}^{old}(0)$ =0.62 from the statistical calculations. If this is combined with the P_3 distribution from HOD taken as P_{local}^{new} , the resulting $P_{1,3}(0)$ is 0.36. This $P_{1,3}(0)$ value, as well as the combined $P_{1,3}$ distribution as a whole, is rather close to the $P_{1,2}^{c}$ distribution from Table III with $P_{1,3}(0)$ =0.42 from the linear surprisal plot. For the OH+GeH₄ reaction with E_{av} =38.4 kcal mol⁻¹, the statistical population is $P_{local}^{old}(0)$ =0.70, and the combined ground stretching state fraction is $P_{1,3}(0)$ =0.29, which again in a good agreement with the linear surprisal result of 0.33 from model I. These findings support the concept of a partial energy release to the old O–H bond in reactions (1)–(3), and, consequently, the distributions labeled $P_{1,2}^{c}$ in Table III seem to be more reliable than those labeled $P_{1,2}^{b}$.

C. Vibrational energy disposal and comparison with X+HBr, HI, and GeH_4 (X=F, CI, and O) reactions

The vibrational distributions of the HF, HCl, and OH products from the reactions of F, Cl, and $O({}^{3}P)$ atoms with

TABLE VI. Comparison of energy disposal for the OH(OD)+HR \rightarrow H₂O(HOD)+R and X+HR \rightarrow HX+R (R=Br, I, GeH₃; X=F, Cl, O) reactions.^a

Reaction	$\langle E_{\rm av} \rangle$ kcal mol ⁻¹	$\langle f_v \rangle$	E_{vs}/E_v^{b}	$-\lambda_{\nu n}^{\ c}$
OH+HBr	33.7	0.61	0.30	4.5
OD+HBr	33.1	0.65	0.61	6.1
OH+HI	49.8	0.36	0.46	-0.9
OD+HI	49.2	0.41	0.31	0.2
$OH+GeH_4$	38.4	0.46	0.41	1.5 - 3.7
OD+GeH ₄	37.8	0.51	0.48	3.5-5.4
F+HBr	51.0	0.60		5.7
Cl+HBr	18.2	0.38		3.0
O+HBr	22.0	0.51		
F+HI	67.2	0.55		4.4
Cl+HI	34.4	0.64		6.2
O+HI	35.4	0.56		d
F+GeH ₄	62.6	0.50		5.5
Cl+GeH ₄	30.0	0.24		2.7
O+GeH ₄	30.0	0.46 ^e		3.4

^aReference 15 for OH(OD)+HBr and Refs. 11, 12, 58 for the atomic reactions.

 ${}^{b}s=2$ (ν_2 mode) for OH and s=3 (ν_3 mode) for OD reactions.

 ${}^{c}n = 1,3 \ (\nu_{1,3} \text{ mode}) \text{ for OH and } n = 3 \ (\nu_{3} \text{ mode}) \text{ for OD reactions.}$

^dNonlinear surprisal if the experimental value is used for P(0); however, OH(v=0) may have a contribution from formation of I(${}^{2}P_{1/2}$) atoms. ^eIf the P(1)/P(0) from Ref. 58 is used, the $\langle f_{v} \rangle$ increases to 0.53.

GeH₄, HI, and HBr have been studied by infrared chemiluminescence¹¹⁻¹⁴ and laser-induced fluorescence ^{57,58} methods. The $\langle f_v \rangle$ and $-\lambda_v$ values are compiled in Table VI. All reactions displayed inverted HX(v) distributions. In the case of the O+HI reaction, the P(0) population of OH was higher than P(1), as obtained by laser-induced fluorescence experiments.¹⁴ If the P(0) point is ignored, the distribution gives a linear surprisal plot. The F atom reactions all give similar results with $\langle f_v \rangle = 0.5 - 0.6$, and they are prototypes for the H-L-H class of dynamics. The Cl atom results are more varied, but care must be taken in the interpretation of the HBr reaction because of the small available energy. Although the rates are much slower, the results for $O({}^{3}P)$ atoms resemble those from F atoms with $\langle f_n(OH) \rangle \approx 0.5$. The linear vibrational suprisal and the $\langle f_v \rangle$ value for O(³P)+GeH₄ are consistent with direct abstraction. The nonstatistical OH λ -doublet population from GeH₄ has been interpreted as evidence for an insertion component.⁵⁸ However, the low P(0)yield and the difficulty of interpretation of λ -doublet distributions⁵⁷ in low J levels make this claim less than certain. The highly inverted vibrational distributions from the $O(^{3}P)$ +HBr and HI reactions are reproduced by guasiclassical trajectory calculations⁵⁹ and they can be understood in terms of a direct abstraction mechanism for a H-L-H mass combination. The similarity of $\langle f_v \rangle$ values for OH(OD) +HBr and F+HBr reactions has previously been noted,¹⁵ and this is why the OH(OD)+HBr is taken as the reference reaction for direct H atom abstraction by OH radicals. In the paragraphs below, the energy disposal and dynamics are summarized for OH(OD)+HI and GeH₄.

We shall first consider reactions of OD, because the P_3 distributions describe the energy disposal to the O–H vibra-

tional mode connected most directly to the reaction coordinate. The values of the mean total vibrational energy, $\langle E_n \rangle$, the mean fraction of the available energy released as HOD vibrational energy, $\langle f_n \rangle$, and the fraction of energy in the O-H stretch mode relative to the total vibrational energy, $\langle E_{3n} \rangle / \langle E_n \rangle$, are given in Table V for reactions (1D)–(3D). The OD+HI reaction has $\langle E_{\nu} \rangle = 20.0 \text{ kcal mol}^{-1}$, which when compared with the available energy of 49.2 kcal mol⁻¹, gives $\langle f_n \rangle = 0.41$; the energy released specifically to the O-H mode is $\langle E_{3v} \rangle = 6.2$ kcal mol⁻¹, corresponding to $\langle E_{3v} \rangle / \langle E_v \rangle = 0.31$. These values are smaller than the corresponding values for the OD+HBr reaction, $\langle f_v \rangle = 0.65$ and $\langle E_{3v} \rangle / \langle E_v \rangle = 0.61$. The OD+GeH₄ reaction is an intermediate case; the $\langle E_n \rangle$ is 19.4 kcal mol⁻¹ and the available energy is 37.8 kcal mol⁻¹, which gives $\langle f_v \rangle = 0.51$. The energy in the O–H vibration is $\langle E_{3n} \rangle = 9.3$ kcal mol⁻¹, corresponding to $\langle E_{3v} \rangle / \langle E_v \rangle = 0.48$. The greater release of energy to $v_1 + v_2$ [0.69 and 0.52 for (2D) and (3D), respectively] rather than to v_3 should be noted.

The fraction of the total vibrational energy released to H_2O is nearly the same as for HOD, but the specific energy release to the new bond is masked by mixing with the local mode of the old O-H bond. The OH+HI reaction with a distribution extending to $v_{1,3}=4$, demonstrates a reduction of vibrational energy; $\langle E_v \rangle = 17.9 \text{ kcal mol}^{-1}$ and $\langle f_v \rangle = 0.36$, compared to $\langle E_v \rangle = 20.6$ kcal mol⁻¹ and $\langle f_v \rangle = 0.61$ for the OH+HBr reaction. This vibrational disposal to H₂O is slightly less than the statistical limit, $\langle f_v \rangle^{\text{st}} = 0.38$, for reaction (2). The energy in just the bending mode of H₂O, $\langle E_{n2} \rangle$, can be assigned for the OH reactions. The $\langle E_{n2} \rangle$ is 8.2 kcal mol⁻¹ for HI reaction, which corresponds to $\langle E_{v2} \rangle / \langle E_v \rangle = 0.46$. This value slightly exceeds the statistical fraction $\langle f_{v2} \rangle / \langle f_v \rangle^{\text{st}} = 0.41$ and the HI reaction has the highest fraction for bending excitation of the three reactions. The mean vibrational energy for the OH+GeH₄ reaction, using the $P_{1,3}(0)=0.33$ deduced from the linear surprisal plot, is equal to $\langle E_v \rangle = 17.7$ kcal mol⁻¹, and $\langle f_v \rangle = 0.46$. This is larger than the statistical value for model I prior, $\langle f_v \rangle^{\rm st} = 0.35$. The energy in the bending vibrations is $\langle E_{v2} \rangle = 7.3$ kcal mol⁻¹, corresponding to $\langle E_{v2} \rangle / \langle E_v \rangle = 0.41$; the statistical value is $\langle f_{v2} \rangle / \langle f_v \rangle^{st} = 0.44$ for model I prior. An interesting feature is the growing fraction of bending energy, $\langle E_{v2} \rangle / \langle E_v \rangle = 0.30$, 0.41, and 0.46 for the HBr, GeH₄, and HI series. This pattern is consistent with a growing component for an addition-migration reaction mechanism.

In summary, the $\langle f_v \rangle$ values for reactions (1)–(3) decrease from a maximum of 0.61–0.65 for HBr, to an intermediate value, 0.46–0.50, for GeH₄, and, to the nearly statistical limit of 0.42–0.43 for the HI reaction. A direct comparison of the energy disposal into the newly formed bond is provided by $\langle E_{v3} \rangle / \langle E_v \rangle$ from reactions of the OD radical. The major part of the vibrational energy, 61%, is concentrated in the new bond by the HBr reaction, indicating the high specificity of the vibrational energy release. For GeH₄ some specificity holds with nearly half of the vibrational energy in the new bond. But for HI, $\langle E_{v3} \rangle / \langle E_v \rangle$ is equal to the statistical limit of one third. The trend of the average values is augmented by the surprisal analysis, where

 $-\lambda_{v3}$ values serve as a measure of deviation from the statistical distribution. The λ_{v3} values are -6.1, -3.1, and ~ 0 for the HBr, GeH₄, and HI reactions, respectively. As the energy release to the new bond declines, the energy in the bending mode increases for these three reactions. We are forced to conclude that in spite of the zero activation energy, the preferred characteristic reaction pathways differ for OH radicals with HBr, HI, and GeH₄. Evidently, obtaining a microscopic understanding of H atom abstraction reactions by OH radicals from various reagents will be more difficult than for F, Cl or O atom reactions.

In retrospect different dynamics for the HBr and HI reactions is not surprising in view of the ability of molecules containing iodine to form complexes with OH radicals^{54,55} and O atoms.⁶⁰⁻⁶² At low initial translational energy, 3.8 kcal mol^{-1} , both IO and HOI products from the $O({}^{3}P)+C_{2}H_{5}I$ reaction emerge from the OIC₂H₅ complex, as has been shown in crossed molecular beam experiments.^{61(a)} The formation of the HOI product arises from the OIC₂H₅ complex through a five-centered ring transition state in which the H atom migrates to the oxygen from the terminal CH₃ group. Vibrationally hot HOI formed via a five-centered transition state was also observed as a product from $O(^{3}P)+C_{2}H_{5}I$, $n-C_{3}H_{7}I$, $(CH_{3})_{2}CHI$, and $(CH_{3})_{3}CI$ reactions.^{60,61} HOI was a major product of the OH+I₂ reaction, and it was also detected in the OH+CH₃I and CH₂I₂ chemical systems by observation of the O-H stretch and bend modes of HOI via a FTIR technique.⁶² The absence of the HOBr product from exoergic the $O(^{3}P)+C_{2}H_{4}Br_{2} \rightarrow HOBr+C_{2}H_{3}Br$ reaction was explained by the location of the five-centered transition state in the exit valley of the potential energy surface, which is inaccessible to collisions with a low initial translational energy.^{61(b)} The nearly statistical vibrational distribution of H₂O from OH+H'I suggests the formation of a HO-I-H' complex with subsequent migration of the H' atom via a threecentered transition state to give H₂O. Migration of a H atom initially bound to the I atom has been observed in $H+IF(IC1) \rightarrow HF(HC1)+I$ reaction, as a second microscopic channel in addition to the direct reaction.⁶³

Additional information is needed before a firm decision can be made about the dynamics for the GeH₄ reaction. Possibly the mechanism is a mixture of direct abstraction and addition-elimination pathways. Trajectory calculations⁸ for the OH+HBr reaction illustrated a difficulty for understanding the mechanism that was responsible for releasing adequate amounts of energy into the water bending mode. Finding a potential energy surface that would give even a higher $\langle f_{2v} \rangle$ in a direct abstraction reaction for OH+GeH₄ would be a difficult challenge.

VI. CONCLUSIONS

The vibrational excitation of the H₂O and HOD molecules formed in the reactions of OH($X^{2}\Pi$) and OD ($X^{2}\Pi$) radicals with HBr, GeH₄, and HI have been studied via analysis of the infrared chemiluminescence accompanying these reactions in a fast-flow reactor at 300 K. Vibrational distributions of H₂O and HOD were obtained by computer simulation of spectra in the 2400–3900 cm⁻¹ range. The spectroscopic simulation for H₂O incorporates the exact line positions for the transitions from levels with $E_v \leq 18000$ cm⁻¹ (51 kcal mol⁻¹). The H₂O emission from the combination $\nu_2 + \nu_3$ bands in the 4500–5500 cm⁻¹ range also was observed; the relative intensity was consistent with the sum intensity for (011) band strength given in HITRAN database. However, a serious disagreement, about a factor of 4, was found between the predicted intensity of the HOD (011) band from the HITRAN database relative to the experimental intensity.

The fraction of the available energy released as H₂O and HOD vibrational energy decreased from 0.65 to 0.41 for the HBr, GeH₄, and HI series, despite the increasing exothermicity and rate constants in the series. The stretching vibrational distribution of H₂O(HOD) was inverted for the HBr reaction in accord with expectation for a direct abstraction reaction. The vibrational energy distribution decreased with increasing E_v , but was still nonstatistical, for the GeH₄ reaction, and the distribution was nearly statistical for the HI reaction. Surprisal analysis of the vibrational distributions indicated a decline in the specific energy release into the newly formed O-H bond for the HBr, GeH₄, and HI series of reactions. Conversely, the release of energy to the bending mode, ν_2 , increased in the series. The specific features of the vibrational distributions from the OH/OD reactions with HBr, GeH₄, and HI permitted the assignment of the mechanisms as direct abstraction in the former case and additionmigration in the latter. The reaction with germane may proceed by both pathways or, less likely, the direct abstraction mechanism has a potential surface that favors excitation of the bending mode, rather than the stretch modes, of water. Based on these three examples, the energy disposal to H₂O(HOD) from OH radical reactions is much more varied than for analogous reactions of F, Cl or O atoms.

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APPENDIX: CALCULATION OF F FACTORS

The intensity of a rotation-vibrational line in absorption may be expressed^{40,41} by

$$I = (\nu/\nu_0) S_{\nu}^0 Lg \exp(-E''/kT) F/Q_R,$$
(A1)

where S_{ν}^{0} is the vibrational band strength, *L* is the rigid rotor transition intensity, *E''* is the lower state rotational energy, *g* is the statistical weight of the lower level, Q_{R} is the rotational partition function, and *F* is the *F* factor. The first-order general expression for the *F* factor is

$$F = \{1 - [U\delta\langle J^2 \rangle + W\delta E(\kappa)]\}^2, \tag{A2}$$

where $\partial \langle J^2 \rangle$ is the difference of J(J+1) for the upper and lower levels, and $\partial E(\kappa) = E'(\kappa) - E''(\kappa)$. Here $\kappa = (2B - A - C)/(A - C)$ is the asymmetry parameter and $E(\kappa)$ is a term in the energy expression for a rigid asymmetric rotor. The constants U and W for the fundamental band of the antisymmetric mode are given by the expression⁴⁰

$$U_{3} = (\alpha_{3}^{xx} + \kappa \alpha_{3}^{yy})/(1+\kappa), \quad W_{3} = (\alpha_{3}^{xx} - \alpha_{3}^{yy})/(1+\kappa),$$
(A3)

where and a_3^{xx} and a_3^{yy} are defined by

$$\alpha_3^{xx} = -\mu_0 / (2\mu_3) \frac{a_{xz}^3}{I_{xx}^{1/2}} \left(\frac{2B}{\widetilde{\omega}_3}\right)^{1/2} \frac{2A}{\widetilde{\omega}_3}$$
(A4)

and

$$\alpha_{3}^{yy} = \frac{\widetilde{\omega}_{3}2C}{\mu_{3}} \left[\frac{\mu_{1}\widetilde{\omega}_{1}}{(\widetilde{\omega}_{1}^{2} - \widetilde{\omega}_{3}^{2})} \frac{\zeta_{13}^{y}}{(\widetilde{\omega}_{1}\widetilde{\omega}_{3})^{1/2}} \right. \\ \left. + \frac{\mu_{2}\widetilde{\omega}_{2}}{(\widetilde{\omega}_{2}^{2} - \widetilde{\omega}_{3}^{2})} \frac{\zeta_{23}^{y}}{(\widetilde{\omega}_{2}\widetilde{\omega}_{3})^{1/2}} \right] \\ \simeq \frac{\widetilde{\omega}_{3}2C}{\mu_{3}} \frac{(\widetilde{\omega}_{2})^{1/2}}{(\widetilde{\omega}_{3})^{1/2}} \frac{\mu_{2}\zeta_{23}^{y}}{(\widetilde{\omega}_{2}^{2} - \widetilde{\omega}_{3}^{2})}.$$
(A5)

Here, z_{13}^{v} and z_{23}^{v} are the Coriolis constants, ω_s is the fundamental frequency of the *s*th mode and $m_s = \partial m/\partial q_s$ is the dipole derivative relative to the normal coordinate q_s . For the water molecule the first term in brackets in Eq. (A5) is much smaller than the second one due to the smaller Coriolis coupling ($z_{13}^{v} = -0.005518$; $z_{23}^{v} = -0.9996$) and dipole derivative ($m_1 = 0.0239$; $m_2 = 0.171$), and it can be neglected despite the smaller denominator.

Following the method described in Ref. 40 and based on the first-order perturbation theory, the *F* factors for the combination bands of the antisymmetric mode were calculated using, instead of the constants a_3^{xx} and a_3^{yy} , new constants, a_{c3}^{xx} and a_{c3}^{yy} , which have the form

$$\alpha_{c3}^{xx} = \alpha_3^{xx} \sqrt{\nu_3}, \quad \alpha_{c3}^{yy} = \alpha_3^{yy} \sqrt{\nu_2 + 1} \sqrt{\nu_3}.$$
 (A6)

At first, F factors were determined for the v_3 fundamental band, using expressions (A4) and (A5). The asymmetry dependent term of the rotational energy, $E(\kappa)$, was obtained as a difference between the actual rotational energy and a common $\frac{1}{2}(A+C)J(J+1)$ value, divided by $\frac{1}{2}(A-C)$. Good agreement with theoretical F factors from Ref. 40 was obtained. Then, during the calculation of the hot and combination bands, the intensity of each rotational transition in a given band was calculated as $I = I_{v3} \cdot F/F_{v3}$, where I_{v3} is the intensity of the same transition in the v_3 fundamental, and F and F_{v3} are the F factors for a given band and v_3 fundamental, respectively. Most of the correction factors, $F/F_{\nu3}$, were in the 0.85-1.3 range, with the largest deviations from the unity being the factors of 2 and 0.5 for some J>5 transitions of the bands with high bending excitation, such as (051) or (052).

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