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Dynamics of the reactions of O(1D) with CD₃OH and CH₃OD studied with time-resolved Fourier-transform IR spectroscopy

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We investigated the reactivity of O(1D) towards two types of hydrogen atoms in CH₃OH. The reaction was initiated on irradiation of a flowing mixture of O₃ and CD₃OH or CH₃OD at 248 nm. Relative vibration-rotational populations of OH and OD (1 ≤ v ≤ 4) states were determined from their infrared emission recorded with a step-scan time-resolved Fourier-transform spectrometer. In O(1D) + CD₃OH, the rotational distribution of OD is nearly Boltzmann, whereas that of OH is bimodal; the product ratio [OH]/[OD] is 1.56 ± 0.36. In O(1D) + CH₃OD, the rotational distribution of OH is nearly Boltzmann, whereas that of OD is bimodal; the product ratio [OH]/[OD] is 0.59 ± 0.14. Quantum-chemical calculations of the potential energy and microcanonical rate coefficients of various channels indicate that the abstraction channels are unimportant and O(1D) inserts into the C−H and O−H bonds of CH₃OH to form HOCH₂OH and CH₃OOH, respectively. The observed three channels of OH are consistent with those produced via decomposition of the newly formed OH or the original OH moiety in HOCH₂OH or decomposition of CH₃OOH. The former decomposition channel of HOCH₂OH produces vibrationally more excited OH because of incomplete intramolecular vibrational relaxation, and decomposition of CH₃COOH produces OH with greater rotational excitation, likely due to a large torque angle during dissociation. The predicted [OH]/[OD] ratios are 1.31 and 0.61 for O(1D) + CD₃OH and CH₃OD, respectively, at collision energy of 26 kJ mol⁻¹, in satisfactory agreement with the experimental results. These predicted product ratios vary weakly with collision energy. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4759619]

I. INTRODUCTION

The reactions of electronically excited oxygen atom O(1D) with hydrocarbons have been the focus of many investigations concerned with atmospheric chemistry. For the simplest system, the reaction of O(1D) + CH₄, several reaction channels that yield products, such as CH₃ + OH, H₂CO/CH₃O + H, and H₂CO/HCO + H₂, have been reported.¹ According to experiments with crossed molecular beams, the branching ratios of these three product channels are ~77%, 18%, and 5%, respectively.¹ A significant proportion of the product OH scattered in the forward and backward directions from the O(1D) beam, indicating that the abstraction channel is important in the channel of formation. The observations of non-statistical vibration-rotational distributions of OH (Refs. 2–8) and CH₃ (Refs. 9 and 10) indicate that they are produced via a path with the lifetime of intermediate CH₃OH⁺ too small to complete the intramolecular vibrational relaxation (IVR).¹¹,12 The H products are noticeably scattered backward, whereas the H₂ products exhibit an isotropic angular distribution; the latter likely arises through a long-lived insertion intermediate. Direct information on the lifetime of the intermediate was given by half-collision experiments through the UV photodissociation of the O₃–CH₄ van der Waals complex;¹³ the largest OH formation interval, 5.4 ps, corresponds to the reaction of the intermediate of which the internal energies are randomized statistically, whereas the smallest formation interval, 0.2 ps, corresponds to direct abstraction. The potential-energy surface (PES) of the O(1D)+CH₄ reaction calculated at a higher level indicates that the path of minimum energy follows a barrierless insertion of O(1D) into the C−H bond to form intermediate CH₃OH and a direct abstraction path through a nearly collinear O−H−C geometry.¹⁴ An additional abstraction path with a small barrier might occur on the electronically excited 2¹Σ⁺ surface. Based on this PES, quasiclassical trajectory calculations assuming the CH₃ group to act as a pseudoatom depict an internal distribution of OH in agreement with the experimental observations.⁵,1⁷

In the reaction of O(1D) with species that possess two types of H atoms, such as methanol (CH₃OH), the reaction paths are expected to be more complicated than those of O(1D) + CH₄. O(1D) might insert into either the C−H or the...
O–H bond, or abstract a H atom directly from the CH$_3$ or OH moiety of CH$_3$OH. Goldstein and Wiesenfeld reacted O(1D) with partially deuterated methanol CH$_3$OD and CD$_2$OH and determined product ratios of [OH]/[OD] from the laser-induced fluorescence (LIF) of OH. These authors reported that ~70% OH product arises from the hydroxyl site, whereas the reactions of O(1D) with the methyl group account for the remaining OH product. This result is in accord with the rate coefficient of the reaction O(1D) + CH$_3$OH reported as 5.1 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which is much greater than the value (1.5 ± 0.4) × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction of O(1D) + CH$_4$. The greater rate coefficient for the reaction of O(1D) with CH$_3$OH than with CH$_4$ was attributed to an increased reactivity of O(1D) towards the OH moiety of CH$_3$OH. Goldstein and Wiesenfeld also determined the vibrational populations of OH($v = 0, 1$) and OD($v = 0–2$) and concluded that an attack on the methyl moiety of methanol generates greater vibrational excitation of hydroxyl radicals than that from attack on the hydroxyl moiety. In these experiments, vibrational states of the product OH or OD beyond $v = 1$ or 2, respectively, were unreported due to the limitation of the LIF method associated with the predissociation of the electronically excited state. Moreover, their reaction system included a buffer gas (He at 10 Torr), precluding information on the rotational distribution of OH; the vibrational distribution of OH might also be affected by collisional relaxation under such conditions. Matsumi et al. detected H atoms with the LIF method and determined a quantum yield of 0.18 for production of H atom in the reaction of O(1D) + CH$_3$OH. These authors reported that [H]/[ID] = 0.26 ± 0.03 and 7.1 ± 0.8 for the reaction of O(1D) with CD$_2$OH and CH$_3$OD, respectively. To explain the selectivity in the formation of product H, two possible mechanisms were considered: (1) insertion of an O atom into the C–H bond is followed by preferential breaking of the new O–H bond because of incomplete IVR in the reaction intermediate, and (2) cleavage of the C–H bond is more likely to occur than of the O–H bond of the reaction intermediate HOCH$_2$OH because the dissociation energy of the former is smaller than of the latter. Despite all these preceding works, information on the rotational distribution and a more complete vibrational distribution of OH is lacking.

Here, we report our observations of rotationally resolved infrared (IR) emission spectra of OH and OD that were produced from the reaction of O(1D) with CH$_3$OD and CD$_2$OH. One advantage of IR emission spectroscopy is the ability to monitor OH and OD in vibration-rotational levels greater than $v = 2$, which are difficult to detect with the LIF method because of predissociation. In addition to the rotational distributions of OH and OD, we determined also the ratio of [OH]/[OD]. We calculated quantum-chemically the PES of various reaction channels and predicted accordingly the branching ratios to assist the interpretation of experimental data.

II. EXPERIMENTS

The apparatus employed to obtain time-resolved emission spectra is based on a step-scan Fourier-transform spectrometer (FTS) that was described previously only a brief summary appears here. For experiments on O(1D) + methanol, ozone (O$_3$), and methanol were injected separately into the reaction chamber. A telescope mildly focused the photolysis beam from a KrF laser (248 nm, 19 Hz) to an area ~12 × 10$^{-2}$ mm$^2$ at the reaction center to yield a fluence of ~53 mJ cm$^{-2}$; this laser beam decomposed O$_3$ to form O(1D). IR emission was collected with two Welsh mirrors (focal length 10 cm), directed into the step-scan FTS, and detected with an InSb detector (Kolmar Technologies) equipped with a preamplifier (rise time 0.34 μs and responsivity 3.2 × 10$^4$ V W$^{-1}$). The transient signal from the InSb detector was further amplified 20 times with a voltage amplifier (Stanford Research Systems, model 560, bandwidth 1 MHz) before being digitized with an external data-acquisition board (12-bit) at 25-ns resolution. Data were typically averaged over 60 laser pulses at each scan step; 4569 scan steps were performed to yield an interferogram resulting in spectra of resolution 0.8 cm$^{-1}$ in a spectral range of 3800–2170 cm$^{-1}$ to cover the emission of OH and OD. For the reaction of O(1D) + CH$_3$OH, 3473 scan steps were performed to yield an interferogram resulting in spectra of resolution 0.5 cm$^{-1}$ in a spectral range of 3650–2950 cm$^{-1}$ to cover emission of OH. To increase further the ratio of signal to noise, five spectra recorded under similar conditions were averaged. The temporal response function of the instrument was determined with a pulsed IR laser beam, as described in Ref. 24. The temporal response period of the detection system is approximately 1 μs, determined with an IR laser emission. The spectral response function was calibrated with a black-body radiation source.

To decrease the collision quenching of OH and OD, a minimal pressure yielding satisfactory signals was used: P$_{O_3}$ = 0.018–0.022 Torr, P$_{CD_2OH}$ = P$_{CH_3OD}$ ± 0.015 Torr. Flow rates were F$_{O_3}$ = 0.7–1.0 sccm, F$_{CD_2OH}$ = F$_{CH_3OD}$ = 3.9–4.5 sccm, in which sccm denotes cm$^3$ min$^{-1}$ under standard conditions (1 atm and 298.15 K). Approximately 60% of O$_3$ was dissociated upon irradiation at 248 nm according to the reported absorption cross section of ~1.1 × 10$^{-17}$ cm$^2$ molecule$^{-1}$ and O(1D) quantum yield of ~0.90 ± 0.05 for O$_3$ at 248 nm and the laser fluence used. The depletion of O$_3$ in the flowing system after each laser pulse was modest, as was confirmed by the negligible variation of the signal intensity when we varied the repetition rate of the photolysis laser from 19 Hz to 30 Hz.

CH$_3$OH (99.9%, Mallinckrodt), CD$_2$OH (isotopic purity 99.5%, Cambridge Isotope Laboratories), and CH$_3$OD (isotopic purity 99%, Cambridge Isotope Laboratories) were employed without further purification. For experiments with CH$_3$OD, the reaction chamber was heated to 373 K under vacuum followed by passivation with D$_2$O (10 Torr) at 298 K for 1 h. After evacuation, the system was filled with D$_2$O (10 Torr) overnight and was treated with passivation and evacuation three times before each experiment. O$_3$ was produced from O$_2$ (Scott Specialty Gases, 99.995%) with an ozone generator (Polymerics, Model T-408) and stored over silica gel at 196 K. The partial pressure of O$_3$ was determined from the absorption of Hg emission at 254 nm in a cell of length 7.0 cm; the absorption cross section of ~1.1 × 10$^{-17}$ cm$^2$ for O$_3$ at 254 nm was used.
III. COMPUTATIONS

A. Potential-energy surfaces and branching ratios

The geometries of reactants, products, intermediates, and transition states on the PES of the O(1D) + CH3OH reaction were optimized with the B3LYP/aug-cc-pVTZ density-functional theory (DFT).27–30 The vibrational wavenumbers were calculated at this level to characterize local minima and the transition state and to correct for the zero-point energy. To obtain reliable energies and predictions of rate coefficients, we calculated single-point energies at the CCSD(T)/aug-cc-pVTZ level based on the structures predicted with B3LYP/aug-cc-pVTZ, expressed as CCSD(T)/B3LYP/aug-cc-pVTZ. For the abstraction channels, whose transition states could not be found by the DFT method, we calculated energies with the MRCI(8,8)//CAS(10,10)/6-311+G(3df,2p) methods.33, 34 Calculations of the intrinsic reaction coordinate55 were performed to connect each transition state with the designated reactants and products. All calculations of electronic structure were performed with the GAUSSIAN 03 (Ref. 36) and MOLPRO programs.37

The minimum energy path (MEP) representing a barrierless insertion or association process was obtained by calculating the potential energy curve at the CASPT2(8,8)/6-311+G(3df,2p)//CAS(8,8)/6-311+G(3df,2p) level of theory along its reaction coordinate: O···H (for C−H or O−H abstraction), O···C (for C−H insertion), or O···O (for O−H insertion) from its equilibrium separation to ~5 Å at step size of 0.1 Å and with other geometric parameters fully optimized. The MEP was fitted to the Morse potential function $E(R) = D_e [1 - \exp(-\beta(R - R_e))]^2$ and employed to approximate the variational transition state in calculations of rate coefficients. In the above equation, $R$ is the reaction coordinate (i.e., the distance for O···H, O···C, or O···O), $D_e$ is the bond dissociation energy excluding zero-point energy, $\beta$ is an exponential factor, and $R_e$ is the equilibrium value of $R$ of an insertion product or an association intermediate. The numbers of states for the tight transition states are evaluated according to the rigid-rotor harmonic-oscillator approximation. The lower vibrational modes in the transition states were treated as classical one-dimensional free rotors. For those paths involving hydrogen atom transfer, Eckart tunneling effects38 were taken into account in the rate coefficient calculations. The employment of the statistical theory in these rate coefficient calculations implies rapid energy redistributions among all internal degrees of freedom.

The rate coefficients for production of H, D, OH, OD, H2O, HOD, and D2O were predicted according to the following method. We employed the variational transition-state theory for the direct abstraction reactions and the variational Rice-Ramsperger-Kassel-Marcus (RRKM) theory39–42 with Eckart tunneling correction for the insertion/decomposition processes using the VARIFLEX code43 by solving the master equation for the formation and removal of the excited intermediates (HOCH2OH* or CH3OOH*). The removal processes include collisional deactivation and various decomposition reactions. Thus the effects of pressure, temperature, isotopic substitution as well as the kinetic energy carried by the O(1D) atom on the formation of individual products can be reliably examined. To obtain rate coefficients at excess energy $E$, the energies of all transition states and intermediates involved in the insertion/decomposition paths were increased by the amount because the excess translational energy can be quantitatively injected into the excited adducts (HOCH2OH* or CH3OOH*) before their isomerization and fragmentation.

The energy increment was fixed at 10 cm$^{-1}$ in all calculations of sums and densities of states using the modified Beyer-Swinehart algorithm.44 For the decomposition with loose transition states, the potential energy paths are approximated with three parts.45 The first part is represented with a Morse function. The second part corresponds to the internal degrees of freedom of the separate fragments and is assumed to be the same as the normal-mode vibrations of the fragments. The third part is the potential energy for the transitional modes, which is described in terms of a set of internal angles with a sum of products of sinusoidal functions. In the RRKM calculations, the L-J values for HOCH2OH and CH3OOH, were approximated with $\sigma = 4.317$ Å and $\varepsilon/\kappa = 450.2$ K.46

B. Einstein A coefficients for vibration-rotational transitions of OH/OD

The rotational states of the OH radical, an open-shell molecule with ground state $X^2\Pi$, consist of two spin sublevels $F_1$ and $F_2$ corresponding to $J = N + 1/2$ and $J = N - 1/2$, respectively; each $J$ level splits into $e$ and $f$ states through the $\Lambda$-doubling. Because the spin uncoupling depends on $J$, OH is intermediate between Hund’s cases (a) and (b). For the assignment of our emission spectra of OH, we referred to the high-resolution data and molecular parameters of OH47,48 and OD.49–51

A diatomic hydride molecule OH has a large rotational constant and the large rotational constant causes a large extent of centrifugal distortion effect on the radial part of the wavefunction that changes significantly the magnitude of the transition dipole moment (the Herman-Wallis effect);52 the Einstein $A$ coefficients must consequently be evaluated for respective vibration-rotational transitions. Nelson et al. derived the electric dipole-moment function of OH from observations of the relative intensities of vibration-rotational transitions of OH.53 Using this function, they calculated the Einstein $A$ coefficients of vibration-rotational transitions according to

$$A(v' J' F' \rightarrow v'' J'' F'') = \frac{16\pi^3}{3\hbar c} \left| \langle v' J' F' | \mu(r) | v'' J'' F'' \rangle \right|^2,$$

(1)

in which $\mu(r)$ is the dipole-moment function and $| v' J' F' \rangle$ is the eigenfunction of the vibration-rotational state of OH in which the $\Lambda$-type splitting is disregarded. To estimate the population distribution of OH in this work, we employed a table of the Einstein $A$ coefficients reported by Holzclaw et al.,54 who calculated the transition dipole moment according to the dipole-moment functions reported by Nelson et al.,53 from the numerical solution of the Schrödinger equation in which the RRK potential was introduced.
IV. RESULTS AND DISCUSSION

A. IR emission from the O(1D) + CD$_3$OH system

Figure 1 shows the time-resolved emission spectra in the spectral regions 2800–3700 and 2160–2650 cm$^{-1}$ recorded at 1-μs intervals for the first 3 μs upon irradiation at 248 nm of a flowing mixture of O$_3$/CD$_3$OH (1/5.3, 0.125 Torr); O(1D) was generated on photolysis of O$_3$ to react with CD$_3$OH. Sharp lines in two groups located in the regions 2800–3700 cm$^{-1}$ and 2160–2600 cm$^{-1}$ are identified, together with two broad feature covering the regions 2160–2350 cm$^{-1}$ with a maximum near 2200 cm$^{-1}$. The first and second groups of sharp lines are readily assigned to the $\Delta v = -1$ transitions of OH and OD radicals, respectively, and the observed broad feature is likely co-products of OH or OD. Because it is difficult to identify positively the carrier of this feature from the available information, we concentrate on the analysis of spectral lines of OH and OD.

The intensities of emission lines of OH and OD rise towards their maxima $\sim 2 \mu$s after irradiation of the flowing sample at 248 nm. Because the initial concentration of CD$_3$OH, $\sim 3.4 \times 10^{15}$ molecule cm$^{-3}$, is much greater than that of O(1D), the condition of pseudo-first-order reaction is valid. The pseudo-first-order rate coefficient $k_1 = 2 \times 10^8$ s$^{-1}$, in which the rate coefficient of O(1D) + CH$_3$OH was reported by Matsumi et al. in accord with the observed rise time for emission of OH or OD. For an improved ratio of signal to noise, we analyzed the distribution of internal states of OH or OD according to the emission spectra averaged over 0–5 μs, and corrected for the small rotational quenching effect, as described later.

The assignments of the observed lines to vibration-rotational transitions of OH and OD, indicated at the top part of Fig. 1, were made according to the high-resolution spectral data for OH (Refs. 47 and 48) and OD:49-51 most lines are associated with transitions of $P_1 (F_1 \rightarrow F_1)$ and $P_2 (F_2 \rightarrow F_2)$ for $\Delta v = -1$ ($v = 1-3$). Lines associated with $R_1$, $R_2$, $Q_1$, and $Q_2$ transitions have much smaller intensity as $J$ increases, consistent with the report by Nelson et al.53,55 Most A doublet $e$ and $f$ lines are unresolved because the resolution was set at 0.8 cm$^{-1}$ in these experiments. For $J \geq 10.5$, the $e/f$ splitting exceeds 1 cm$^{-1}$, resulting in broadened lines or partially resolved lines. In this experiment, we made no attempt to separate the populations of the $e$ and $f$ transitions, but used the total population for each vibration-rotational transition. To analyze these observed lines, we assumed a Gaussian shape for each line and performed curve fitting on each line, including overlapped lines.

To improve the ratio of signal to noise in these experiments, the micropopulation was determined from spectral lines integrated for 0–5 μs after photoirradiation. Each vibration-rotational line in the $P$ branch was normalized with the instrument spectral-response function, and divided by its respective Einstein coefficient to yield a relative population $P_v(v', J', F')$. In Fig. 2, the logarithm of the micropopulation in a rotational state ($v'$, $J'$, $F'$), defined as $P_v(v', J', F')(2J'+1)$, is plotted as a function of the rotational energy that is defined as the average of the $e$ and $f$ term values from which the vibrational term value is subtracted. The micropopulations of the $F_1$ and $F_2$ components are similar, as indicated in
As shown clearly in Fig. 2, the rotational distribution of OH is not singly exponential, whereas that of OD is nearly exponential (Boltzmann). Average rotational energies for each vibrational level of OH and OD, $E_r(v)$, were obtained on summing the product of rotational level energy and normalized population over all observed rotational levels. The average rotational energy $E_r$ was derived on multiplying the observed $E_r(v)$ with the respective vibrational population, to be discussed later. The average rotational energies $E_r$ of OH and OD are thus calculated to be $11 \pm 3$ and $5 \pm 1$ kJ mol$^{-1}$, respectively; $E_r$ of OD is much smaller than that of OH.

For OD, we derived rotational temperatures ($T_R$) of $470 \pm 60$, $450 \pm 50$, $440 \pm 50$, and $430 \pm 40$ K for $v = 1-4$, respectively. Because the rotational distributions of OH($v = 1$) and OH($v = 2$) are non-Boltzmann, we fitted them with biexponential functions and derived the rotational temperatures $450 \pm 90$ K ($v = 1$) and $400 \pm 40$ K ($v = 2$) of the low-J component and $1100 \pm 110$ K ($v = 1$) and $680 \pm 110$ K ($v = 2$) of the high-J component. For OH($v = 3$), we could fit only a rotational temperature of $420 \pm 10$ K because of the limited levels observed. The population ratio of the high-J component to the low-J component is $\sim 35/65$. Because the spectra were integrated for $0-5$ $\mu$s, the rotational temperatures reflect the average value in this period.

To derive the nascent rotational energy, we estimated the quenching effects by measuring the rotational temperature as a function of time. By integrating the observed lines at 1-μs intervals, we determined the rotational temperature of OD and the high-J and low-J components of OH as a function of time. The rotational temperatures of OD($v$) determined at 1-μs intervals are shown in Fig. 3. The nascent rotational temperatures of $570 \pm 190$ K, $560 \pm 100$ K, and $560 \pm 60$ K were derived for OD($v = 1-3$), respectively, after a short extrapolation to $t = 0$. According to this measurement of the rotational quenching, we estimated that the nascent rotational temperature should be multiplied by $1.2 \pm 0.1$ for OD, compared with those determined for $0-5$ $\mu$s. Using a similar method, we

![FIG. 2. Semilogarithmic plots of the rotational populations of OH and OD as a function of the rotational energy in respective vibrational levels formed from the O(1D)+CD$_3$OH reaction. Average period is 0–5 $\mu$s.](image)

![FIG. 3. Plot of rotational temperature of OD ($v = 1–3$) as a function of time. The data extrapolated to $t = 0$ are indicated with o.](image)
estimated that the nascent rotational temperature should be multiplied by 1.2 ± 0.1 for the low-J component of OH, and 1.8 ± 0.3 and 2.1 ± 0.4 for the high-J component of OH (v = 1 and 2), respectively, compared with those determined for 0–5 μs. We hence estimate the average nascent rotational energies to be 6 ± 2 kJ mol⁻¹ for OD and 18 ± 5 and 6 ± 2 kJ mol⁻¹, respectively, for the high-J and low-J components of OH; the energy of the high-J component is less accurate because of the large factor of correction. After correction for quenching, the population ratio of the nascent high-J component to the low-J component is ∼50/50; the nascent average rotational energy of OH is thus 12 ± 4 kJ mol⁻¹, as listed in Table I.

The relative vibrational populations were derived on counting levels up to the observed maximal J values in each vibrational level, ΣJ,F P(v′, J, F)’. We normalized the values of ΣJ,F P(v′, J, F)’ associated with each vibrational state to yield a relative vibrational population (v’ = 1) : (v’ = 2) : (v’ = 3) : (v’ = 4) for OH and (v′ = 1) : (v′ = 2) : (v′ = 3) : (v′ = 4) for OD

In our IR chemiluminescence experiments, it is impossible to obtain directly information about the population of the vibrational ground state; the population of v′ = 0 was hence estimated on extrapolation from the populations of levels v′ ≥ 1 assuming a Boltzmann distribution. The populations of v′ = 0 relative to v′ = 1 were thus derived to be 2.4 ± 0.3 and 1.5 ± 0.2 for OH and OD, respectively. After renormalizing, we derived vibrational distributions of OH as (v’ = 0) : (v’ = 1) : (v’ = 2) : (v’ = 3) : (v’ = 4) = 56.8 : 23.7 : 14.6 : 4.9 and of OD as (v’ = 0) : (v’ = 1) : (v’ = 2) : (v’ = 3) : (v’ = 4) = 34.1 : 23.0 : 18.9 : 14.9 : 9.1. These vibrational distributions of OH and OD are shown in Fig. 4(a).

The observed ratios of total populations of OH (v = 1–3) and OD (v = 1–4) are derived to be ∼50/50. When we include the estimated populations for the v = 0 levels of OH and OD, the total ratios of populations of OH (v = 0–3) and OD (v = 0–4) are derived to be (61 ± 9)/(39 ± 9) = 1.56 ± 0.36. This ratio is slightly smaller than, but within the error limit of, the ratio (71 ± 12)/(29± 12) = 2.45 ± 1.01 determined from OH (v = 0) and OD (v = 0–2) by Goldstein and Wiesenfeld. The discrepancy is partly due to the fact that their observations were limited to populations in small vibrational levels of OH and OD. As seen from Fig. 4(a), the populations of OD (v > 2) contribute much more significantly than those of OH (v ≥ 2). Using this distribution of vibrational populations, we calculated the average vibrational energies of OH and OD to be 28 ± 6 and 43 ± 8 kJ mol⁻¹, respectively, as listed in Table I. The vibrational energy of OH is slightly smaller than that of OD; in contrast, the rotational energy of OH is greater than that of OD.

**B. Infrared emission from the O(1D) + CH₃OD system**

To discriminate the reaction sites of O(1D) towards the methyl and hydroxyl groups in methanol, we investigated also the reaction O(1D) + CH₃OD. In the reaction of O(1D) + CH₃OD, the channels that produce OH and OD correspond
from the line intensities integrated for 0–5 μs are shown as a function of rotational energy in Fig. 6. The rotational distributions of OH are nearly singly exponential as in the case of OD produced from the reaction of O(1D) + CD₂OH. In contrast, the rotational distributions of OD are biexponential, similar to those of OH from the reaction O(1D) + CD₂OH. The result is in accord with the expectation for such isotopic substitutions. Following a method similar to that described in Sec. IV A, the average rotational energies of OH and OD for the period 0–5 μs are thus calculated to be 5 ± 1 and 9 ± 2 K mol⁻¹, respectively, as listed in Table I.

For OH, we derived rotational temperatures of 410 ± 50, 440 ± 70, and 410 ± 50 K for v = 1–3, respectively. We fitted the rotational distributions of OD(v = 1) and OD(v = 2) with biexponential functions and derived the rotational temperatures 250 ± 20 K (v = 1) and 280 ± 20 K (v = 2) of the low-J component and 990 ± 320 K (v = 1) and 920 ± 400 K (v = 2) of the high-J component. For OD(v = 3), we could fit only a rotational temperature of 350 ± 20 K for the low-J component because of the limited levels observed. The ratio of the high-J component to the low-J component of OD is ~48/52. Because the spectra were integrated for 0–5 μs, the rotational temperatures reflect the average value during this period.

According to measurements of rotational quenching we estimated that the nascent rotational temperature should be multiplied by 1.3 ± 0.2 for OH, 1.2 ± 0.2 for the low-J component of OD, and 1.3 ± 0.3 for the high-J component of OD, respectively. We hence estimate the average nascent rotational energy to be 6 ± 2 kJ mol⁻¹ for OH, and 14 ± 3 and 5 ± 2 kJ mol⁻¹, respectively, for the high-J and low-J components of OD. After correction for quenching, the population ratio of the nascent high-J component to the low-J component is ~50/50; the average rotational energy of OD is thus 10 ± 3 kJ mol⁻¹, as listed in Table I.

We normalized the values of Σ_f' P(v', J', F') associated with each vibrational state to yield a relative vibrational population (v' = 1) : (v' = 2) : (v' = 3) : (v' = 4) = 32.8 : 28.0 : 21.5 : 17.7 for OH and (v' = 1) : (v' = 2) : (v' = 3) : (v' = 4) = 45.9 : 32.1 : 15.8 : 6.2 for OD. The population of v' = 0 is estimated on extrapolation from the populations of levels v' ≥ 1 according to the Boltzmann distribution; the populations of v' = 0 relative to v' = 1 were thus derived to be 1.3 ± 0.2 and 2.3 ± 0.5 for OH and OD, respectively. After renormalizing, we derived the vibrational distributions of OH as (v' = 0) : (v' = 1) : (v' = 2) : (v' = 3) : (v' = 4) = 51.4 : 22.3 : 15.6 : 7.7 : 3.0. These vibrational distributions of OH and OD are shown in Fig. 4(b).

The observed ratios of total populations of OH (v = 1–3) and OD (v = 1–4) are derived to be 46/54. When we include the estimated populations for the v = 0 levels of OH and OD, the ratio of total populations of OH (v = 0–3) and OD (v = 0–4) become (37 ± 9)/(63 ± 9) = 0.59 ± 0.14. This ratio is slightly larger than the ratio (30 ± 6)/(70 ± 6) = 0.43 ± 0.09 reported by Goldstein and Wiesenfeld. Part of the discrepancy arises because their observations are limited to populations in levels v = 0 and 1 of OH and OD. As seen from Fig. 4(b), the populations of OH (v ≥ 2) contribute
to channels that produce OD and OH, respectively, in the reaction of O(1D) + CD₂OH.

The time-resolved IR emission spectra observed at 1-μs intervals from the O(1D) + CH₃OD system are shown in Fig. 5. Similar to the reaction of O(1D) + CD₂OH, two groups of sharp lines located in regions of 3700–2800 and 2650–2160 cm⁻¹ are assigned as the Δν = −1 vibration-rotational transitions of OH and OD, respectively. In addition, broad emission bands are evident in the regions of 3600–3200, 3100–2350, and 2350–2160 cm⁻¹ that might have originated from the co-products of OH or OD, likely CH₂DO or CH₃O. Compared with the spectra of OH and OD in the reaction system of O(1D)+CD₂OH, the line intensities are smaller for both OH and OD and the distributions of internal states differ. The relative rotational micropopulations of the respective vibrational states of OH and OD determined
much more significantly than that of OD \((v \geq 2)\). The determined ratio \([\text{OH}]/[\text{OD}] = 0.59 \pm 0.14\) in \(\text{O}(1D) + \text{CH}_3\text{OD}\) is, notably, practically the same as the inverse of the value \([\text{OH}]/[\text{OD}] = 1.56 \pm 0.36\) observed for \(\text{O}(1D) + \text{CD}_3\text{OH}\).

Using this distribution of vibrational populations, we calculated the average vibrational energies of \(\text{OH}\) and \(\text{OD}\) to be \(65 \pm 15\) and \(27 \pm 5\) kJ mol\(^{-1}\), respectively, listed in Table I. The vibrational energy of \(\text{OH}\) is larger than that of \(\text{OD}\); in contrast, the rotational energy of \(\text{OD}\) is greater than that of \(\text{OH}\).

C. Potential-energy surface and branching of the \(\text{O}(1D) + \text{CH}_3\text{OH}\) reaction

A simplified figure showing only the important reaction paths that produce \(\text{OH}\) and \(\text{H}\) is shown in Fig. 7. A more complete scheme of PES including other product channels is available in Fig. S-2 of the supplementary material.\(^{56}\) The \(\text{O}(1D) + \text{CH}_3\text{OH}\) reaction is initiated according to two mechanisms – insertion and abstraction. The insertion process can proceed via two paths: into a \(\text{C} \cdots \text{H}\) bond to form \(\text{trans-\text{HOCH}_2\text{OH}}\) with exothermicity of \(634\) kJ mol\(^{-1}\) and into the \(\text{O} \cdots \text{H}\) bond via the \(\text{CH}_3\text{O(O)}\text{H}\) association complex lying \(190\) kJ mol\(^{-1}\) below the reactants, to give rise to \(\text{CH}_3\text{OOH}\) with the total exothermicity of \(373\) kJ mol\(^{-1}\) via a small insertion barrier of \(20\) kJ mol\(^{-1}\) (TS1/2s in Fig. 7). One of the MEP curves for the \(\text{C} \cdots \text{H}\) insertion reaction is shown in Fig. S-3 of the supplementary material.\(^{56}\) \(\text{Trans-\text{HOCH}_2\text{OH}}\) can isomerize to \(\text{cis-\text{HOCH}_2\text{OH}}\) with a barrier \(\sim 13\) kJ mol\(^{-1}\). Both energized \(\text{trans-\text{HOCH}_2\text{OH}}\) and \(\text{CH}_3\text{O(O)}\text{H}\) can further decompose to form \(\text{H, OH, and H}_2\text{O}\) via various channels. The direct paths for \(\text{H}\) abstraction can proceed via two channels: attacking the \(\text{CH}_3\) moiety to form \(\text{CH}_2\text{OH} + \text{OH}\) (\(\text{H}_2\)-abstraction) or attacking the \(\text{OH}\) moiety to form \(\text{CH}_3\text{O} + \text{OH}\) (\(\text{H}_2\)-abstraction); both abstraction reactions proceed via shallow pre-reaction complexes (LMa and LMb) and transition-states (TSa and TSb) that have energy within \(1\) kJ mol\(^{-1}\) of the reactants (see Fig. 7). The structures of \(\text{CH}_3\text{O(O)}\text{H, CH}_3\text{OOH, HOCH}_2\text{OH,}\) and related transition states, predicted with the B3LYP/aug-cc-pVTZ method, are shown in Fig. 8.

The production of \(\text{OH}\) and \(\text{OD}\) in the reaction \(\text{O}(1D) + \text{CH}_3\text{OD}\) was investigated for the following dominant channels:

\[
\text{O}(1D) + \text{CH}_3\text{OD} \rightarrow \text{HOCH}_2\text{OD}^* \text{ (C} \cdots \text{H insertion),}
\]

\[
\begin{align*}
\text{HOCH}_2\text{OD}^* & \rightarrow \text{CH}_2\text{OD} + \text{OH} \\
\text{HOCH}_2\text{OD}^* & \rightarrow \text{CH}_2\text{OD} + \text{OD} \\
\text{HOCH}_2\text{OD}^* & \rightarrow \text{CH}_3\text{O} + \text{OD}
\end{align*}
\]

A more complete mechanism including channels for production of \(\text{HOD, DOD, and HOH}\) from decomposition of \(\text{HOCH}_2\text{OD}^*\) is available in the supplementary material.\(^{56}\) For the reaction of \(\text{O}(1D)\) with \(\text{CH}_3\text{OH}\) at room temperature, the predicted total rate coefficient, 4.8
FIG. 7. Simplified potential-energy scheme for production of OH and H in the reaction O(1D) + CH₃OH computed with the CCSD(T)//B3LYP/aug-cc-pVTZ method. TS indicate transition states. Energy is in kJ mol⁻¹.

$10^{-10}$ cm³ molecule⁻¹ s⁻¹, is in agreement with the experimental value of $(5.1 \pm 0.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. About 88% of the reaction occurs by C–H insertion, 11% by O–H insertion, and the rest by direct abstraction from a C–H bond; the negligible contribution from abstraction from the O–H bond is expected according to the predicted potential energy profiles presented in Fig. 7. For the direct abstraction processes, the effect of the multiple reflections above the pre-reaction complexes LMa and LMB have been included; the effect of the reflections might reduce predicted rate coefficients by as much as a factor of 2 at $T < 200$ K (depending on the temperature) and have a negligible effect above 500 K. The abstraction channels are unimportant because they have tight transition states, TSa and TSb, with the energies of −0.8 and 0.8 kJ mol⁻¹, respectively, relative to reactants, whereas the two insertion channels dominate because they are barrierless with less restriction on the configuration of the collisions. At temperatures below 1000 K, the total rate coefficients and the OH product branching ratio were found to be weakly dependent on temperature and independent of pressure below 10 atm because of the large excess energy carried by the insertion products and the small molecular size involved.

For the reaction of O(1D) + CD₃OH, the following paths for production of OH and OD are possible:

\[
\text{O}(^{1}\text{D}) + \text{CD}_3\text{OH} \rightarrow \text{DOCD}_2\text{OH}^* \quad \text{(C–D insertion),} \\
\text{DOCD}_2\text{OH}^* \rightarrow \text{CD}_2\text{OH} + \text{OD} \quad \text{fission of new C–O bond),} \quad \text{(R8)}
\]

\[
\text{CD}_3\text{OH}^* \rightarrow \text{CD}_3\text{O} + \text{OH} \quad \text{fission of O–O bond),} \quad \text{(R12)}
\]

\[
\text{O}(^{1}\text{D}) + \text{CD}_3\text{OH} \rightarrow \text{CD}_2\text{OH} + \text{OD} \quad \text{(D\text{C}-abstraction),} \quad \text{(R13)}
\]

\[
\text{O}(^{1}\text{D}) + \text{CD}_3\text{OH} \rightarrow \text{CD}_2\text{O} + \text{OH} \quad \text{(H\text{O}-abstraction).} \quad \text{(R14)}
\]
The effect of isotopic substitution on the formation of various products can be readily evaluated with separate calculations on the system’s vibrational frequencies and moments of inertia based on the predicted PES. The predicted individual rate coefficients for OH and OD production at room temperature from the O(1D) reactions with CH₃OD and CD₃OH as a function of the kinetic energy are presented in Figs. 9(a) and 9(b), respectively. The initial average kinetic energy of O(1D) that is produced upon photolysis of O₃ at 248 nm was determined to be 36 kJ mol⁻¹ in the laboratory coordinates. In the center-of-mass coordinates of the collision of O(1D) with CH₃OD or CD₃OH, the kinetic energy is 25.5 or 25.9 kJ mol⁻¹.

The predicted results reveal one major OH (k₂) and two OD (k₃ and k₅) production channels in the O(1D) + CH₃OD reaction and one OD (k₅) and two OH (k₁₀ and k₁₂) production channels in the O(1D) + CD₃OH reaction. For O(1D) + CH₃OD, the rate coefficient for OH/OD production is dominated by k₂ and k₃ (insertion of O into the C–O bond followed by rupture of the new and old C–O bonds); k₅ is slightly greater than k₂ at low collision energies but they become comparable (~8.0 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) at collision energies greater than 26 kJ. The rate coefficients k₃ and k₅ remain nearly constant for higher energies because of the large exothermicity of these reaction channels. The bimolecular rate coefficient k₉ (insertion of O into the O–D bond, followed by rupture of the O–O bond) remains nearly constant (5.2 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) throughout the energy range 0–60 kJ mol⁻¹ and is ~0.65 times k₂ and k₃ for energies at 26 kJ mol⁻¹; reaction (R5) is the only dominant channel from the O–H insertion. For O(1D) + CD₃OH, the rate coefficient for production of OH/OD is also dominated by k₉ and k₁₀ (insertion of O into the C–D bond before fission of the OH and OD groups); k₉ is about 1.3 times k₁₀ at low collision energy but become comparable at 60 kJ mol⁻¹. k₁₂ (insertion of O into the O–H bond, followed by rupture of the OH group), similar to k₉, remains nearly constant (4.8 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) in the 0–60 kJ energy range; it is about 63% of k₁₀ and 50% that of k₉ at 26 kJ mol⁻¹.

The ratios of k₀/k₁₀ from the reactions O(1D) + CH₃OD/CD₃OH, shown in Fig. 10, were calculated according to these rate coefficients. For the reaction O(1D) + CH₃OD, k₀/k₁₀ = k₂/k₅ ≃ 0.51, whereas for the reaction O(1D) + CD₃OH, k₀/k₁₀ = (k₁₀ + k₁₂)/k₉ ≃ 1.23 at E = 0 kJ mol⁻¹. These ratios increase gradually and become 0.61 and 1.31, respectively, at 26 kJ mol⁻¹, in satisfactory agreement with the experimental results of 0.59 ± 0.14 and 1.56 ± 0.36. Similarily, we calculated also the ratios of k₀/k₉ for the reaction O(1D) + CH₃OD according to the reactions

\[
\text{HOCH₂OD}^* \rightarrow \text{OCH₂OD} + \text{H (fission of new O–H bond),} \tag{R15}
\]

\[
\rightarrow \text{OCH₂OH} + \text{D (fission of old O–D bond),} \tag{R16}
\]

\[
\rightarrow \text{HOCHOD} + \text{H (fission of C–H bond),} \tag{R17}
\]
and for the reaction $O(1D) + CD_2OH$ according to the reactions

$$\text{DOCD}_2\text{OH} \rightarrow \text{OCD}_2\text{OH} + D \quad \text{(fission of new O–D bond), } \quad \text{(R18)}$$
$$\rightarrow \text{OCD}_2\text{OD} + H \quad \text{(fission of old O–H bond), } \quad \text{(R19)}$$
$$\rightarrow \text{DOCD}_2\text{OH} + D \quad \text{(fission of C–D bond).} \quad \text{(R20)}$$

The O–H insertion product, CH$_3$OOH*, which accounts for only 11% of the insertion/decomposition processes as aforementioned, decomposes mainly by breaking its weak O–O bond to form OH radical. As shown in Fig. 11, the ratio of $k_{15}/k_{13} = (k_{15} + 2k_{17})/k_{15}$ predicted with RRKM calculations for the reaction $O(1D) + CH_3OD$ decreases from 4.1 to 3.3 as the excess energy increases from 0 to 60 kJ mol$^{-1}$, whereas the ratio of $k_{16}/k_{13} = k_{17}/(k_{13} + k_{20})$ for the reaction $O(1D) + CH_3OD$ increases from 0.23 to 0.27. These values are insensitive to the temperature or the kinetic energy carried by the O atom, again attributable to the large amount of energy carried by the insertion products. At the collision energy of 26 kJ mol$^{-1}$, the ratios are 3.9 for $O(1D) + CH_3OD$ and 0.23 for $O(1D) + CD_3OH$.

**D. Mechanism for formation of OH and OD**

According to our theoretical calculations, the abstraction channels are unimportant. For the insertion channels, two intermediates are possible: HOCH$_2$OH from insertion into the C–H bond and CH$_3$OOH from insertion into the O–H bond. The formation of HOCH$_2$OH is supported by the observation of this species in an UV-irradiated Ar matrix containing O$_3$ and CH$_3$OH. The CH$_3$OOH intermediate has not been identified directly.

The observation of bimodal rotational distributions for OD and Boltzmann distribution for OH produced from the $O(1D) + CH_3OD$ reaction indicates that the reaction might proceed via three major channels. This experimental observation is consistent with the predicted mechanism that has a single channel for formation of OH, reaction (R2), and two channels for formation of OD, reactions (R3) and (R5). Similarly, the observation of a Boltzmann rotational distribution for OD and a bimodal rotational distribution for OH in the reaction $O(1D) + CD_2OH$ is consistent with the predicted mechanism that has a single channel for formation of OD, reaction (R9), and two channels for formation of OH, reactions (R10) and (R12).

For the reaction $O(1D) + CH_3OD$, the observed OH has greater vibrational energy than OD, whereas the additional rotational component of OD has greater rotational excitation than OH and the low-J component of OD. Similarly, for the reaction $O(1D) + CD_2OH$, the observed OD has greater vibrational energy than OH, whereas the additional rotational component of OH has greater rotational excitation than OD and the low-J component of OH. These results indicate that the fission of the O–O bond of CH$_3$OD and CD$_2$OOH, reactions (R5) and (R12), produces the hydroxyl radical with smaller vibrational energy but greater rotational energy. The bond angle $\angle$HOO in CH$_3$OOH is 100.6°, whereas the bond angle $\angle$COH in trans-HOCH$_2$OH is 108.5° (Fig. 8). Considering the torque angle during bond fission, one would expect that the OH produced from CH$_3$OOH receives greater rotational excitation than that from HOCH$_2$OH, consistent with experimental observations.

Regarding the vibrational excitation of the hydroxyl radical product, as described above, we observed that the hydroxyl radical produced from the methyl moiety has vibrational excitation greater than that from the hydroxyl moiety of methanol. In the case of $O(1D) + CD_2OH$, the vibrational energy of OD is about 20% of the reaction energy, which is more than the statistical partitioning if one considers the complexity of the co-product CD$_2$OH. This fact indicates that the reaction does not proceed through a long-lived intermediate. There are two possibilities for the observed extensive vibrational excitation for the hydroxyl radical produced from the methyl moiety. One mechanism is that $O(1D)$ abstracts directly one H atom from the methyl group, as was observed in the reaction $O(1D) + CH_4$. In the reaction $O(1D) + CH_4$ in crossed molecular beams, a large proportion of the OH product scatters in the forward direction because of direct abstraction, and OH had much more vibrational than rotational excitation. The second mechanism is that when the reacting O atom, indicated as O*, inserts into the H–C bond of the CH$_3$ moiety, the newly formed HO*–C bond breaks more rapidly than the original C–OH bond; that is, $k_2 > k_3$ and $k_9 > k_{10}$. This condition implies that the lifetime of a portion of the HO*CH$_2$OH intermediate is too small for complete IVR, consistent with the conclusion derived from comparison of observed and calculated [OH]/[OD], to be discussed later. The reaction energy thus becomes localized near the newly formed bond upon insertion of $O(1D)$ into the H–C bond, and highly vibrationally excited O*H is produced quickly. Some HO*CH$_2$OH survives to allow energy redistribution before the fission of the C–OH bond to form less vibrationally excited OH. Both elimination channels from HOCH$_2$OH likely produce OH with little rotational excitation because of a smaller torque angle as indicated above.
A similar non-equilibrium reaction of O(1D) was reported for the reaction \( ^{16}\text{O}(1D) + \text{H}_2\text{O} \rightarrow ^{16}\text{OH} + ^{18}\text{OH} \) in which \(^{18}\text{OH}\) is from the newly formed moiety, whereas \(^{16}\text{OH}\) is a part of the original reactant.60–66 The product \(^{16}\text{OH}\) was found to be highly vibrationally excited, whereas \(^{18}\text{OH}\) was vibrationally much cooler. This condition indicates that the hydroxyl radical products derive their origin on the reaction \( \text{O}(1D) \) for the reaction \( \text{O}(1D) + \text{CH}_3\text{OD} \), the product ratio is \( \text{[OH]} / \text{[OD]} = 0.59 \pm 0.14 \). This indicates that the hydroxyl radical products derive their H or D atoms preferably from the hydroxyl site of methanol. However, because insertion of the O atom into the C–H bond might be followed by fragmentation of the original hydroxyl moiety, listed as reactions (R3) and (R10), these product ratios do not necessarily indicate the preference of the reaction of \( \text{O}(1D) \) with the hydroxyl moiety over the methyl moiety of methanol. In fact, the calculations predicted that about 88% of the reaction occurs by C–\( \text{H} \) insertion and 11% by O–\( \text{H} \) insertion.

In the reaction of \( \text{O}(1D) + \text{CH}_3\text{OD} \), the ratio of \( \text{[OH]} / \text{[OD]} \) depends mostly on \( k_{\text{OH}} / k_{\text{OD}} = k_2(k_3 + k_5) \) according to reactions (R1)–(R5) listed in Sec. IV C. In the reaction of \( \text{O}(1D) + \text{CD}_3\text{OH} \), the ratio of \( \text{[OH]} / \text{[OD]} \) depends on \( k_{\text{OH}} / k_{\text{OD}} = (k_{10} + k_{12}) / k_9 \). If one ignores the kinetic isotopic effects, \( k_9 \approx k_2 \) for fission of the newly formed C–O bond, \( k_{10} \approx k_3 \) for fission of the old C–O bond, and \( k_{12} \approx k_5 \) for fission of the O–O bond. Hence, the ratio of \( \text{[OH]} / \text{[OD]} \) for the reaction \( \text{O}(1D) + \text{CH}_3\text{OD} \) is expected to be approximately the inverse of the \( \text{[OH]} / \text{[OD]} \) ratio for the reaction \( \text{O}(1D) + \text{CD}_3\text{OH} \). Our observed values of \( \text{[OH]} / \text{[OD]} \) are 0.59 for the reaction \( \text{O}(1D) + \text{CH}_3\text{OD} \) and \( \text{[OH]} / \text{[OD]} = 1.56 \) for the reaction \( \text{O}(1D) + \text{CD}_3\text{OH} \) are consistent with this scheme; these observed ratios indicate that \( k_5 \approx k_9 \) and \( k_3 \approx k_{10} \). Without considering the kinetic isotope effect, one would expect that \( k_2 \approx k_3 \) and \( k_9 \approx k_{10} \), if IVR is much more rapid than bond fission. If the bond rupture is more rapid than energy randomization, one would expect that \( k_5 / k_3 \) and \( k_9 / k_{10} \) becomes greater than 1.

At the center-of-mass collision energy of 26 \text{kJ mol}^{-1} for \( \text{O}(1D) \) with methanol, the ratio of \( \text{[OH]} / \text{[OD]} \) is \( k_{10} + k_{12} / k_9 = 1.31 \), predicted for \( \text{O}(1D) + \text{CD}_3\text{OH} \) such that energy is randomized before bond rupture, is slightly smaller than our experimental value of 1.56 ± 0.36; the value of \( \text{[OH]} / \text{[OD]} \) is 1/(0.4 ± 0.2) reported by Goldstein and Wiesenfeld has a large error.18 These results are consistent with the condition in which the breaking of the newly formed C–O bond is more rapid than the breaking of the old C–OH bond in DOCD_2OH such that observed \( k_9/k_{10} \) is greater than prediction. Similarly, the ratio of \( k_{10} / k_9 \) is predicted to be 0.61 for \( \text{O}(1D) + \text{CH}_3\text{OD} \). This predicted value is in close agreement with our experimental value of 0.59 ± 0.14; both are greater than the value of 0.43 reported by Goldstein and Wiesenfeld.19 Considering possible errors, this result is not inconsistent with the condition in which IVR is slower than the bond rupture such that the breaking of the newly formed C–OH bond is more rapid than the breaking of the old C–OD bond in HOCH_2OD, i.e., observed \( k_9/k_{10} \) is greater than prediction; the slower IVR was indicated by the observation of vibrationally excited OH, as discussed above.

The reported experimental value of \( \text{[H]} / \text{[D]} = 7.1 \pm 0.8 \) for \( \text{O}(1D) + \text{CH}_3\text{OD} \) at room temperature19 is much larger than the value of \( k_9/k_{10} = (k_{15} + 2k_{17})/k_{16} = 3.90 \) predicted according to the microcanonical rate coefficients at \( E = 26 \text{kJ mol}^{-1} \). On the other hand, for \( \text{O}(1D) + \text{CD}_3\text{OH} \), the observed ratio of \( \text{[H]} / \text{[D]} = 0.26 \pm 0.03 \) (Ref. 19) is in agreement with the value of \( k_9/k_{10} = k_{19}/(k_{18} + 2k_{20}) = 0.23 \) predicted according to the microcanonical rate coefficients insensitive to the collision energies from 0–60 \text{kJ mol}^{-1}. The much larger discrepancy might indicate that the rate of bond rupture for formation of H or D atoms is much more rapid than IVR. The IVR rates of the skeletal modes involving the O–H bond are much smaller than those of the C–O bonds; the former are associated with formation of H, whereas the latter are with formation of OH. Furthermore, part of the discrepancy might be accounted for by secondary decomposition of OCH_2OD, HOCH_2O, and HOCHOD products.

According to our calculated rate coefficients, the quantum yields for production of H (and D) and OH (and OD) are 0.158 and 0.548 for the reaction \( \text{O}(1D) + \text{CH}_3\text{OD} \) and 0.186 and 0.540 for the reaction \( \text{O}(1D) + \text{CD}_3\text{OH} \). Matsumi et al. reported a quantum yield of 0.18 for production of H atom in the reaction of \( \text{O}(1D) + \text{CH}_3\text{OH} \), consistent with our calculation.

V. CONCLUSION

By monitoring the IR emission of products OH and OD with a step-scan Fourier-transform infrared spectrometer, we investigated the reactions \( \text{O}(1D) + \text{CD}_3\text{OH/CH}_3\text{OD} \). For the reaction of \( \text{O}(1D) + \text{CH}_3\text{OD} \), the nascent average rotational energies are estimated to be 6 ± 2 and 12 ± 4 \text{kJ mol}^{-1} and the average vibrational energies are 43 ± 8 and 28 ± 6 \text{kJ mol}^{-1} for OD and OH, respectively. Product OD is vibrationally more excited than OH, whereas OH shows a bimodal rotational distribution with the additional component having greater rotational excitation than OD. The product ratio \( \text{[OH]} / \text{[OD]} \) is estimated to be 61/39 = 1.56.

For the reaction \( \text{O}(1D) + \text{CH}_3\text{OD} \), the nascent rotational energies are estimated to be 6 ± 2 and 10 ± 3 \text{kJ mol}^{-1} and the average vibrational energies are 65 ± 15 and 27 ± 5 \text{kJ mol}^{-1} for OH and OD, respectively. Product OH is vibrationally more excited than OD, whereas OD shows a bimodal rotational distribution with the additional component having greater rotational excitation than OH. The product ratio \( \text{[OH]} / \text{[OD]} \) was estimated to be 37/63 = 0.59, nearly the inverse of that of the reaction \( \text{O}(1D) + \text{CD}_3\text{OH} \).

The experimental observations are explicable according to a mechanism of \( \text{O}(1D) + \text{CH}_3\text{OD} \) involving two insertion intermediates, HOCH_2OD and CH_3OOD, and three major decomposition channels, reactions (R2), (R3), and (R5). Insertion of \( \text{O}(1D) \) into the C–H bond to form HOCH_2OD followed by fission of the newly formed HO–C bond, reaction (R2), produces vibrationally more excited OH because
of incomplete IVR, whereas fission of the old C−OD bond in HOCH2OD, reaction (R3), produces OD with less vibrational excitation. Insertion of O(1D) into the O−D bond to form CH2COOD followed by fission of the O−O bond, reaction (R5), produces OD with greater rotational excitation, likely due to a large torque angle during dissociation. A similar mechanism applies for O(1D)+ CD3OD: two insertion intermediates, DOCD2OH and CD3OOH, and three decomposition channels, reactions (R9), (R10), and (R12), are involved.

For O(1D)+ CH2OD, the observed ratio of [OH]/[OD] = 0.59 ± 0.14 is close to the value of 0.61 predicted according to microcanonical rate coefficients. For O(1D)+ CD2OH, the observed ratio of [OH]/[OD] = 1.56 ± 0.36 is also close to the predicted value of 1.31. The small deviations are likely due to incomplete IVR.

For O(1D)+ CD2OH, the observed ratio of [H]/[D] = 0.26 ± 0.03 is close to the predicted value of 0.23. For O(1D)+ CH2OD, the reported observed ratio of [H]/[D] = 7.1 ± 0.8 is much larger than the value of 3.90 predicted according to microcanonical rate coefficients. The much larger discrepancy might indicate that the rate of bond rupture for formation of H or D atoms is much more rapid than IVR. Part of the discrepancy might be accounted for by secondary decomposition reactions of OCH2OD, HOCH2O, and HOCH2OH*, subsequent dissociation occurs for both the formed intermediates, DOCD2OH and CD3OOH, and three decomposition channels, reactions (R9), (R10), and (R12), are involved.

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See supplementary material at http://dx.doi.org/10.1063/1.4759619 for calculated Einstein $A$ coefficients of OD, the $A$ coefficient for Meinel band of OD, and a more complete PES and reaction mechanism for O($^1D$) + CH$_3$OH.


