OH-Stretching Overtone Induced Dynamics in HSO$_3$F from Reactive Molecular Dynamics Simulations

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$^*$Supporting Information

**ABSTRACT:** The OH-stretch induced dynamics in fluorosulfonic acid (HSO$_3$F) is characterized from a statistically significant number of trajectories using multisurface adiabatic reactive molecular dynamics (MS-ARMD) simulations. The global reactive potential energy surface, which describes H-transfer and HF-elimination, is parametrized at the MP2/6-311G++(2p,2d) level of theory with an accuracy of better than 1 kcal/mol. Excitation along the OH-local mode leads to H-transfer dynamics but elimination of HF is only observed for excitations with $\nu \geq 6$ for 1 out of 5000 trajectories. This finding differs fundamentally from the situation for vibrationally induced photodissociation of H$_2$SO$_4$ and HSO$_3$Cl, for which, even with excitations of 4 quanta along the OH-stretch mode, elimination of H$_2$O and HCl, respectively, is readily observed on the subnanosecond time scale. RRKM rates for HX-elimination in HSO$_3$X (X = F, Cl) only differ by a factor of 5. The findings from the reactive molecular dynamics simulations together with the RRKM results thus indicate that the origin for a closed HF-production channel is dynamical. This is also consistent with experimental findings for hydrofluoroethanes in shock tubes, which found pronounced non-RRKM behavior.

**INTRODUCTION**

The study of decomposition products from energized molecules in the atmosphere is of great practical relevance. In the troposphere, interaction of stable and reactive species with sunlight leads to a myriad of decomposition products which are involved in a rich chemistry. Of particular importance are reactions and their decomposition products which lead to long-living, harmful (re)agents and those which affect the ozone layer. A topical example is the formation of sulfur-containing compounds from decomposition of H$_2$SO$_4$, which are involved in acid rain and aerosol formation in the tropo- and stratosphere and are significant for the chemistry of the atmosphere. As H$_2$SO$_4$ cannot decay along a thermal and electronically driven pathway in the atmosphere, alternative reaction mechanisms needed to be considered. It was suggested$^{2}$ and later confirmed$^{3-6}$ that a vibrationally induced mechanism can drive the H$_2$SO$_4$ $\rightarrow$ SO$_3$ + H$_2$O reaction. In additional, vibrationally induced reactivity has also been investigated in mode-selective chemistry.$^{7,8}$

Vibrational overtone induced reactions also differ in their reaction kinetics from thermally driven reactions. Population of higher vibrational states leads to a nonequilibrium preparation of the system from which it usually decays in a nonstatistical, non-RRKM (Rice–Ramsperger–Kassel–Marcus) fashion. This differs from electronic excitation that typically can be analyzed within an RRKM framework. One topical example for vibrationally induced reactivity is the photodissociation of pyruvic acid.$^{9,10}$ For this system it was demonstrated that if the decomposition reaction is initiated through pumping of the OH-stretch vibration, the kinetics does not follow an RRKM scheme, unlike the thermally induced reaction. This is important as the chemistry following a thermally or vibrationally driven process differs. The thermal process generates methylhydroxycarbene, which subsequently can isomerize to acetaldehyde. Contrary to that, vibrational overtone excitation produces relatively stable high-energy methylhydroxycarbene radicals that can drive further reactions through collisions with other collision partners, such as water.$^{11}$

In the atmosphere, vibrationally excited molecules can undergo unimolecular reactions before vibrational quenching occurs due to collisions with surrounding material.$^{12-14}$ Especially X–H stretching (X = O, C, N) induced reactivity, which shows high vibrational frequencies compared to those of other bonds, are of significance.$^{12,14}$ A well studied example is the dissociation of HNO$_x$. Here the atmospheric relevance is related to releasing NO$_2$, which affects ozone formation.$^{12,15,16}$ Other examples of atmospherically important molecules that undergo vibrationally induced dissociation include pyruvic...
and HO$_2$NO$_2$. Including vibrationally induced reactivity leads to improved atmospheric models. One example is formation of atmospheric aerosols, which influences the climate, due to hydrophilic acids and alcohols in the atmosphere. Excluding vibrational overtone-induced photodissociation leads to incorrect particle sizes.

The present study investigates the vibrationally induced reactivity of HSO$_3$F. Unlike the atmosphere of Earth, the Venusian atmosphere includes, as an important minor gas, hydrogen fluoride (HF) in its mesosphere. HF is highly soluble in H$_2$SO$_4$ and small amounts of it can react with H$_2$SO$_4$ which has a concentration of about 80% in Venus’ clouds, to form fluorosulfonic acid (HSO$_3$F) and water. It was also suggested that HSO$_3$F may be a proxy for the reaction of HF with water forms hydrofluoric acid (HF) in its mesosphere. The present computations are based on multisurface adiabatic reactive molecular dynamics (MS-ARMD) simulations. MS-ARMD can treat multiple reaction pathways, accessible to HSO$_3$F (Figure 1).

![Figure 1. Graphical representation of the possible reaction paths for fluorosulfonic acid (HF-elimination, elimination; intramolecular H-transfer, H-transfer; HF-elimination after intramolecular H-transfer, indirect elimination), including atom numbering used here.](image)

Atomic color code: S, yellow; O, red; F, pink; H, white.

**COMPUTATIONAL DETAILS**

**MD Simulations.** All MD simulations were carried out with CHARMM, using multisurface adiabatic reactive molecular dynamics (MS-ARMD). Starting from an optimized structure (10 000 steps of adopted Newton–Raphson), each system was individually heated to 300 K for 40 ps. Next, the systems were equilibrated for 40 ps at 300 K, followed by free dynamics. The time step in all simulations was $\Delta t = 0.1$ fs to conserve energy and account for the rapid hydrogen vibrational motion. The equations of motion were propagated using the leapfrog Verlet algorithm.

For the vibrational excitation, the instantaneous velocity vector was scaled along the OH-normal mode vector such as to deposit the appropriate amount of energy corresponding to a particular vibrational excitation into the molecule. After such a nonequilibrium preparation, the system was propagated in the (NVE) ensemble and the dynamics was analyzed in terms of (i) intramolecular hydrogen transfer from one oxygen to another one (H-transfer) or (ii) elimination of HF.

**Parametrization of the Force Field.** The parametrization of the force fields for each state $V(x)$ (i.e., connectivities), necessary for describing the reaction of HSO$_3$F, was accomplished by fitting the FF parameters to reference ab initio energies, calculated at the MP2/6-311++G(2d,2p) level of theory using Gaussian09. To obtain a meaningful description of the four different states, three permutation invariant configurations of HSO$_3$F and one state describing the elimination products (HF and SO$_3$), the standard CHARMM harmonic bond potentials were replaced by Morse potentials. Furthermore in the elimination products the standard CHARMM Lennard-Jones potential between H/F and the SO$_3$ atoms where replaced by generalized Lennard-Jones potentials (see ref 6). The remaining FF terms were calculated as in conventional CHARMM, i.e., harmonic angle potentials in combination with Urey–Bradley terms, dihedral terms (for HSO$_3$F), additional improper dihedral potentials for SO$_3$, and point charges. After the individual parametrization of each state, the obtained FFs were combined by using energy dependent, normalized weights ($w(x)$) to the states $V(x)$. To realistically describe the shape and energetics in the crossing regions between two states, smoothing functions (Gaussian times polynomial functions, GAPOs) are used.

$$V^r_{\text{GAPO},i}(x) = \exp\left(-\frac{(V^r_0(x) - V^r_{0,k})^2}{2\sigma^2_{ij,k}}\right) \sum_{i=1}^{m_{ij}} a_{ijkl}(\Delta V^r_i(x) - V^r_{0,k})^j$$

They suitably modify the shape of the reactive potentials on the basis of the difference of the potential energy of two states ($\Delta V^r = V(x) + V(x)$) to reproduce the energies from ab initio calculations (i.e., IRC calculations) in the barrier region. The center and width of the Gaussian function are given by $V^r_0$ and $\sigma_{ij,k}$, respectively. The order of the polynomial is given by $m_{ij}$, $a_{ijkl}$ is the coefficient of the polynomial. The global PES is then given by the sum of the weighted sum of PESs and the weighted sum of the GAPOs.

$$V_{\text{MS-ARMD}}(x) = \sum_{i=1}^{n} w_i(x) V_i(x) + \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} [w_i(x) + w_j(x)] \sum_{k=1}^{m} \Delta V^r_{\text{GAPO},i}(x)$$

Parametrization of the individual states $V(x)$ started with initial parameters obtained from SwissParam. Representative structures of the reactant and the product were sampled from 500 ps MD simulations at 300 K. For these structures, reference energies were determined at the MP2/6-311++G(2d,2p) level of theory. The fitting of the individual FFs for each state was performed using a downhill simplex algorithm. For the parametrization of the GAPOs the IRCs of the two possible reaction mechanisms (hydrogen transfer and HF-elimination) were also calculated at the MP2/6-311++G(2d,2p) level of theory. For fitting the parameters of the GAPOs a genetic algorithm was used, as their functional form leads to a highly nonlinear fit.

**RESULTS AND DISCUSSION**

**Quality of the Force Field.** The parametrization of the reactant and product states was performed in an iterative fashion. Starting with a set of 100 structures for HSO$_3$F and
SO₃ + HF a first fit for the two states was carried out. This was followed by further MD simulations using this improved set of parameters from which another 500 structures was extracted and included in the fit. Following several similar rounds of refinements, the fit of the individual states included 5200 reference points in total. The root mean squared deviation for the final set between the target and the fitted energies was 0.93 and 0.58 kcal/mol, respectively, for the HSO₃F and SO₃ + HF state (blue and green points in Figure 2). The energies of the

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Figure 2. Energy correlation of 4865 MP2/6-311++G(2d,2p) reference structures and the fitted FF. Color code: blue = HSO₃F, green = SO₃ + HF, orange = IRC elimination, red = IRC H-transfer, yellow = 500 structures of HSO₃F from 100 ns simulation, cyan = additional HSO₃F and SO₃ + HF. Top left inset shows the ab initio IRCs (black circles, calculated with MP2/6-311++G(2d,2p)) and fitted FF (red curves, including fitted GAPOs). (A) HF-elimination. (B) Intramolecular H-transfer. Bottom right inset shows the energy correlation for 200 structures of HSO₃F (blue) and 11 points around the MP2 elimination IRC calculated with B3LYP/6-311+G(2d,2p) and MP2/6-311++G(2d,2p).

IRC structure were calculated with these states V(x) and provided to the GAPO fit procedure. For the parametrization of the elimination reaction, a RMSD of 0.30 kcal/mol was achieved (Figure 2A) using three Gaussians, one with polynomial order up to four and two with polynomials up to order five. For H-transfer three pure Gaussian GAPOs yield a RMSD of 0.63 kcal/mol (Figure 2B).

Table 1. Calculated OH Bond Stretching Frequencies of HSO₃F (kcal/mol)²

<table>
<thead>
<tr>
<th>νOH</th>
<th>MS-ARMD</th>
<th>CC-VSCF on MP2/TZP¹³</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>41.41</td>
<td>39.06</td>
</tr>
<tr>
<td>5</td>
<td>50.43</td>
<td>49.53</td>
</tr>
<tr>
<td>6</td>
<td>59.14</td>
<td>61.47</td>
</tr>
<tr>
<td>7</td>
<td>67.52</td>
<td>75.20</td>
</tr>
<tr>
<td>8</td>
<td>75.59</td>
<td>N/A</td>
</tr>
</tbody>
</table>

²MS-ARMD values are compared to CC-VSCF frequencies calculated at the MP2/TZP level of theory."¹³

The reaction probabilities ranged from 75% for νOH = 4 to 98% for all higher excitations. For νOH = 4, 33% of the trajectories showed only one single H-transfer within 2.5 ns after which intramolecular energy redistribution precluded further reactions. Excitations with 5 and more quanta always lead to multiple hydrogen transfers during the 2.5 ns.

MS-ARMD follows reactions explicitly in time and hence recrossing after transit of the transition state is possible. Such recrossing is also observed here. When residence times of the hydrogen atom on a particular oxygen are analyzed, events with lifetimes shorter than 500 fs are excluded. Residence times τ of the hydrogen transfer has occurred were analyzed separately. The expectation values ⟨τ⟩ = ∫ τp(τ) dτ for the first hydrogen transfer to occur is 890.6, 449.3, 117.3, and 55.0 ps for excitations with νOH = 4 to 7. After the first transfer, the average residence times are 357.8, 89.9, 27.6, and 12.0 ps, respectively. The residence time distributions p(τ) for excitation with νOH = 5 before the first transfer and p(τ) for all subsequent H-transfer events are shown in Figure 3. Here it is found that the first H-transfer occurs after ≈100 ps with a broad distribution extending up to 1.7 ns. After the first transfer, the residence times follow an exponentially decaying

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Figure 3. Normalized residence probability distribution p₁(τ) before the first H-transfer takes place for HSO₃F (black solid) and for HSO₃Cl (black dashed). Raw data for the distribution of all subsequent H-transfer events p₁,τ(τ) for HSO₃F (red diamonds) follow a single exponential decay (blue solid line) and raw data for HSO₃Cl (red dashed) are similar but the distribution is wider and is shifted to somewhat longer time scales. The reaction in the top right corner shows one of the two possible first H-transfer reactions (from O₄ to O₃). The subsequent H-transfer reaction, which was considered for determination of the residence time, is shown in the bottom right corner. Backward (bwd) reaction from O₃ to O4 and forward (fwd) reaction from O₃ to O₂.
distribution (red trace in Figure 3). This is likely to be related to the fact that once H-transfer occurred (i.e., the necessary energy is in the relevant reaction coordinate) the probability for back-transfer is large (~60% of the events). For the first H-transfer to occur the efficiency of energy flow into the relevant reaction coordinate is the rate limiting step, which depends directly on the initial conditions.

Figure 3 shows the $P(\tau)$ and the residence time distribution for HSO3Cl when $\nu = 5$ is excited. The first hydrogen transfer event in HSO3Cl takes place immediately after excitation and shows a slight secondary maximum around 700 ps. The average residence times before the first transfer for excitation with $\nu = 4$–6 are 573.5, 242.1 (black, dashed line in Figure 3), and 65.2 ps for HSO3Cl, which are shorter by close to a factor of 2 compared to those for HSO3F despite a similar barrier height for the H-transfer reaction. After the first transfer has occurred, residence times are slightly longer for HSO3Cl than for HSO3F.

**HF-Elimination Reaction.** Next, HF-product formation was considered. For any of the excitations with $\nu_{OH} = 4$, 5, and 6 none of the 5000 independent trajectories showed elimination. Excitation levels of $\nu_{OH} = 4$–6 correspond to an increase in the internal energy between 40 and 60 kcal/mol, which is considerably higher than the barrier for HF-elimination, which is 35.1 kcal/mol. As mentioned above, most trajectories exhibit H-transfer, which is a potential channel for efficient energy redistribution such that recurrence times can become very long. To validate this, 10 trajectories with $\nu_{OH} = 6$ were extended up to 100 ns. However, none of these trajectories showed HF-elimination. For a broader assessment, $10^5$ independent trajectories were run from initial structures generated from a Monte Carlo simulation where structures were saved every 20000 MC steps. After a short heating, equilibration and dynamics (each 10 ps) MS-ARMD simulations with $\nu_{OH} = 6$ were performed in the same manner as explained above. None of these trajectories showed elimination within 100 ps.

In an attempt to force HF-elimination, 5000 additional trajectories were run with excitation of $\nu_{OH} = 7$ and 500 trajectories with excitation $\nu_{OH} = 8$, respectively. Product formation was found in five and eight cases for the two excitation levels. Hence, the reaction probability is excessively small despite the large energy deposited compared with the barrier of 35.1 kcal/mol for the elimination reaction. This points toward the importance of couplings between internal degrees of freedom to move from reactant to product in the present case, a point that will be considered further below.

The finding that the reaction probability for HF-elimination is negligible prompted us to consider the possible reasons in some more detail. First, the minimum energy and transition state geometries for the HX-elimination reaction are compared. One notable difference between the two transition state structures is the OH bond length, which is 1.21 Å for HSO3F compared to 1.27 Å for HSO3Cl (Figure 4). This suggests that the chlorinated complex has a weakened OH-bond compared to the fluorinated species. The other coordinates either are similar (such as valence angles) or can be explained by the larger size of Cl vs F.

Next, the reaction dynamics in HSO3X (X = F and Cl) was compared. First, it is noted that even for moderate excitation levels ($\nu_{OH} = 4$) along the OH-stretch coordinate HCl-elimination in HSO3Cl occurs for 15% of the trajectories on a 2.5 ns time scale. This compares with no elimination at all for HSO3F for the same level of excitation and over the same time interval after vibrational excitation. The computed MP2/6-311++G(2d,2p) barriers for HX-elimination and H-transfer for the two systems are 35.1 kcal/mol vs 35.1 kcal/mol and 38.1 kcal/mol vs 38.1 kcal/mol for HSO3F and HSO3Cl, respectively.

Given the similar barrier heights for the two systems, it is meaningful to explicitly compare the molecular dynamics of trajectories that do and do not show HX-elimination, respectively. To this end, 2-dimensional probability distributions from trajectories with vibrationally excited ($\nu_{OH} = 5$) HSO3F and HSO3Cl were considered; see Figures 5 and 6 for several combinations of internal degrees of freedom. This particular level of excitation was chosen because for HSO3Cl a large fraction of trajectories (more than 90%) show HCl-elimination and, at the same time, a statistically sufficient number of nondissociative trajectories exists from which probability distributions can be constructed.

Comparison of the normalized probability distributions $P(\phi), P(\theta), P(\phi, \theta)$, and $P(\phi, \theta, \varphi)$ (where $\phi$ is the $X=\mathrm{S}-\mathrm{O}-\mathrm{H}$ dihedral angle) from simulations for HSO3F and HSO3Cl is shown in Figure 5. As is evident, noneliminating trajectories do not sample these regions in configuration space whereas those leading to the product evidently do sample the crossing geometries for HSO3Cl.
probability distribution functions for HSO₃F resemble very closely those for noneliminating HSO₃Cl. These distributions suggest that the relevant degrees of freedom are those sampled in the dissociative trajectories but not in the nondissociative trajectories. These are the S−O−H angle and the X−S−O−H dihedral angle. Additionally, a minor contribution arises from the F−S−O angle.

The difference in configuration space sampled by non-dissociative and dissociative HSO₃Cl trajectories can also be seen from the TS distribution of dissociative HSO₃Cl trajectories (red crosses in Figure 5). The TS has a coplanar structure (dihedral angle Cl−S−O−H ≈ 0°; see bottom structures in Figure 4). Furthermore, it is noticeable that for dissociation the S−O−H angle needs to be smaller than its equilibrium value of 110° (HSO₃Cl panel 4, Figure 5). Likewise, the Cl−S−O angle takes smaller values in the TS than in the reactant conformation (HSO₃Cl panel 3, Figure 5).

The bottom of Figure 5 shows some notable HSO₃Cl structures that are sampled for nondissociating trajectories. The two different synperiplanar conformations of the reactant (I and II) as well as the two different H-transfer product conformations. Panels 1 and 3 in all four rows in Figure 5 show two maxima that simultaneously sample configuration III (in both conformations) together with I and configuration IV (in both conformations) together with II. In panels 2 and 4 in all rows the three configurations can be identified. In panels 2 the distributions at short O−H distances correspond to I and II, those at longer O−H distances (>1.5 Å) correspond to III and...
IV separated by their different dihedral angle distribution. Furthermore, in panel 2 the two synperiplanar conformations I and II can be identified by the $X=S-O-H$ dihedral angle ($X = F, Cl$). This is similar for panel 4, where small $S-O-H$ angles correspond to structures III and IV, whereas the two maxima for bigger $S-O-H$ angles correspond to I and II.

The probability distributions of $P(r_{SO})$ with $X$ being F and Cl, respectively, are shown in Figure 6. The nondissociative trajectories of HSO$_3$F and HSO$_3$Cl are circular, whereas dissociative trajectories of HSO$_3$Cl sample longer $S-Cl$ distances in combination with shorter Cl$-S-O$ angles, therefore tending toward the TSs. Structurally, the shorter angle decreases the distance between Cl and H, while the longer $S-Cl$ distance favors the S$-Cl$ bond breaking. These conformations appear to be inaccessible in HSO$_3$F.

From these probability distributions (Figures 5 and 6) it can be seen, by comparing the phase space sampled, that coupling between the OH-stretch and SOH-bend, XOS-bend, SX-stretch, and the torsion XSOH ($X = F, Cl$) is crucial for OH-stretching overtone induced photodissociation.

To better characterize the region around the transition state, umbrella sampling simulations were carried out for the HF-elimination reaction. These simulations used the ratio $\rho = r_{SO}/r_{OH}$ as the reaction coordinate. The reaction coordinate was scanned from $\rho = 0.5$ to $\rho = 3.0$, and the data were combined using the weighted histogram analysis method (WHAM). The barrier is 38.5 kcal/mol, compared with a forward activation energy of 35.1 kcal/mol. The transition state (TS) is located at $\rho = 1.685$, i.e., for $\rho < 1.685$ the system is in its reactant state whereas for $\rho > 1.685$ the product is formed. To verify its nature, an umbrella sampling simulation 12.5 ns in length was carried out and 1750 representative structures were used as starting points for energy minimization which were free to evolve toward product or reactant, respectively. The fraction of structures relaxing toward reactant and product was 57% and 43%, respectively, which suggests that the ensemble characterizes the TS in a meaningful way. However, further refinement to obtain the point with a committor probability of 0.5 would, in principle, be possible but was not pursued here. The averaged structure over these 1750 samples is reported in the inset in Figure 7. The normalized probability distributions of $P(\phi_{SO})$, $P(\phi_{FOM})$, and $P(\phi_{ZFSO})$ for all 1750 samples are shown in Figure 5 (red distribution in the first row).

Comparison of the distributions $P(\angle FSOH, ZFSOH)$ and $P(\angle SOH, ZFSO)$ from HSO$_3$F (red distribution in the first row) and dissociative HSO$_3$Cl (fourth row) in Figure 5 shows that the sampling of the angle SOH is around 10$^\circ$ smaller in HSO$_3$F compared to that for HSO$_3$Cl. The harmonic frequencies of the SOH bending and the XSOH torsion in the two systems are 1149 cm$^{-1}$ vs 1141 cm$^{-1}$ and 219 cm$^{-1}$ vs 258 cm$^{-1}$ for HSO$_3$F and HSO$_3$Cl, respectively. In addition, the Fourier transform of the power spectrum for these excitations in HSO$_3$F and HSO$_3$Cl were calculated from 100 ps of equilibrium MD simulations. Anharmonic frequencies for the SOH bending of HSO$_3$F and HSO$_3$Cl were found to be at 1157 and 1148 cm$^{-1}$, respectively. The XSOH torsion is 307 and 353 cm$^{-1}$ for HSO$_3$F and HSO$_3$Cl.

Additional insight into the reaction mechanism may be obtained from an RRKM analysis of the HX-elimination pathway for both HSO$_3$X ($X = F$ and Cl) systems. For this, harmonic frequencies for the global minimum (Table S1) and the TS for HSO$_3$F and HSO$_3$Cl were determined at the MP2/6-311++(2d,2p) level of theory and RRKM rates were computed by using the MultiWell program. The potential energies of the dissociated products relative to the reactants are 7.99 and 7.89 kcal/mol for HSO$_3$F and HSO$_3$Cl, respectively. A collision free regime was assumed and tunneling was neglected. For the energy range equivalent to an excitation with $\nu = 4-6$ it was found that the RRKM rates for HSO$_3$F are only a factor of 5 smaller than the rate for HSO$_3$Cl. Such a small difference indicates that the differences for HX-elimination in HSO$_3$F and HSO$_3$Cl found in the reactive MD simulations are not predominantly a statistical but rather a dynamical effect.

Finally, the coupling between different internal modes was probed from simulations started at the transition state of the elimination reaction with zero temperature and evolving toward the reactant. The power spectrum along the OH-stretching coordinate indicates that the number of modes to which this degree of freedom couples is considerably larger in HSO$_3$Cl than in HSO$_3$F. This suggests that coupling to softer degrees of freedom in HSO$_3$F is less efficient, which renders transfer of the OH-stretching energy into modes that promote the system toward the HF-elimination product more difficult.

Ab Initio MD. For a final validation of the findings concerning a small probability for HF-elimination, ab initio MD simulations were carried out. For this, “Atom Centered Density Matrix Propagation” (ADMP$^{36,39}$) molecular dynamics as implemented in Gaussian09 was employed. ADMP uses an extended Lagrangian approach and Gaussian basis functions for propagation of the density matrix.

The simulations were carried out at the B3LYP/6-311+G(2d,2p) level of theory. Coordinates and velocities (after overtone excitation with $\nu_{OH} = 6$) were taken from the ensemble of structures utilized in the MS-ARMD simulation. The level of excitation was chosen to increase the probability to
observe elimination within a few picoseconds of simulation time. The temperature was set to 300 K.

To validate the use of the B3LYP/6-311+G(2d,2p) level of theory, the energies for 200 representative HSO₃F structures around the reactant and transition state were calculated and compared with energies from MP2/6-311++G(2d,2p) calculations. Furthermore, the energy of the TS from the IRC calculation from MP2, as well as five points before and five points after the TS along the IRC path were included in the comparison. The RMSD between B3LYP and MP2, both with 6-311+g(2d,2p), is 0.4. The regression coefficient of the linear fit is 0.94. The energy correlation between both methods is shown in the bottom right inset in Figure 2. It is found that B3LYP/6-311+G(2d,2p) is a meaningful level of theory for ADMP simulations.

ADMP simulations were carried out for 20 ps with a time step of Δt = 0.2 fs. Only 1 out of the 43 trajectories exhibited HF-elimination after 9.5 ps. The trace of this trajectory (dark green) in terms of the HF and SF distances sampled is shown in Figure 7. This can be compared with HF and SF distances sampled by an ADMP trajectory without elimination (light green) and an MS-ARMD trajectory without elimination (blue) for the same degree of excitation. As is evident, when the HF and SF distances are considered, no noticeable differences between the three trajectories are found. Figure 7 furthermore shows the normalized F–H and S–F distance distribution from 4891 MS-ARMD simulations with νOH = 6 (black lines). The three traces in Figure 7 lie well within the distribution of the νOH = 6 MS-ARMD trajectories.

This can be compared with HF and SF distances sampled by an ADMP trajectory without elimination (light green) and an MS-ARMD trajectory without elimination (blue) for the same degree of excitation. As is evident, when the HF and SF distances are considered, no noticeable differences between the three trajectories are found. The trace of the dissociative trajectory is also shown in Figure 5 (green crosses in row two).

**Discussion and Conclusion.** Vibrationally induced reactions are important in a number of circumstances as they differ in fundamental ways from thermally induced reactions. In particular, they can exhibit mode specificity and nonstatistical behavior. Decomposition reactions following vibrational OH-excitation have been found for species such as H₂SO₄, HONO, or HSO₃Cl. In all these cases it is known that energies between 30 and 60 kcal/mol are required to drive the reaction, which implies that higher overtones need to be excited if a vibrationally driven process is envisaged. However, due to their small cross sections (3–6 orders of magnitude smaller than electronic transitions at the same energy), product yields in laboratory experiments from vibrationally induced reactions are small, almost independent of the quantum yield. In the atmosphere, the photodissociation rate depends not only on the (wavelength dependent) cross section and the quantum yield but also on the actinic flux which is, however, almost constant (at 10¹⁸ photons cm⁻² s⁻¹) over the relevant energy range for vibrational excitations of 4–6 OH-quanta but may vary with altitude.

The HF-yield from OH-stretch excitation of HSO₃F is found to be negligible (1 out of 5000 trajectories for νOH ≥ 6). This sets it apart from similar (and related) systems such as H₂SO₄, HONO, or HSO₃Cl using the same approach. For both, H₂SO₄ and HSO₃Cl, it was found that after 500 ps more than 50% of the trajectories lead to H₂O- or HCl-elimination, respectively, for νOH = 6. Together with the observation that the excitation cross section for vibrational overtones is intrinsically small and decrease by approximately 1 order of magnitude with each quantum of excitation, HF-production from OH-stretch induced photodissociation of HSO₃F is suppressed compared to the cases for H₂SO₄ and HSO₃Cl. Hence, HSO₃F is not a meaningful proxy in laboratory studies to study vibrationally induced photodissociation of compounds such as H₂SO₄.

The present findings of pronounced non-RRKM behavior are also consistent with earlier studies that considered HF-elimination from hydrofluorooethanes in shock tube experiments at elevated temperatures (1600–2400 K). In particular, the decomposition of CF₃CH₃ → CH₂CF₂ + HF has been considered to be “the most unambiguous example of an intrinsic” non-RRKM unimolecular process.

The present analysis also suggests that coupling between radial and softer (torsional and angular) degrees of freedom is essential for promoting an elimination reaction in such systems. This is consistent with previous ab initio MD simulations (PM3) that found the excitation along the OH local mode yields HF-elimination in 0 to 1 (out of 32) trajectories for νOH = 5–7. The yield increases to 7 up to 25 (out of 48) if 1 quantum of SOH bending is excited together with excitation of the OH-stretch. However, exciting 1 quantum of the O–S–O–H torsion together with the OH-stretch also increases the number of trajectories with HF-elimination (9 to 21 out of 48). Finally, these results are also consistent with the observation that in elevated temperature (∼400 K), near-IR gas phase measurements for HSO₃F are more stable than those for HSO₃Cl.

In conclusion, the present work shows that HF-production from OH-stretching overtone induced photodissociation of HSO₃F is insignificant. Following vibrational excitation with 4 and more quanta along the OH local mode, intramolecular H-transfer is the dominant reaction channel. A comprehensive characterization of vibrationally induced HF-elimination in
HSO3F can be carried out due to exhaustive sampling, which is possible because MS-ARMD simulations allow us to run a statistically significant number of trajectories for sufficiently long simulation times. The analysis points toward the importance of the coupling between radial and angular/dihedral degrees of freedom to promote reactivity in such systems.

ASSOCIATED CONTENT

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Notes

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