

## Weakly Bound Molecules in the Atmosphere: A Case Study of HOOO

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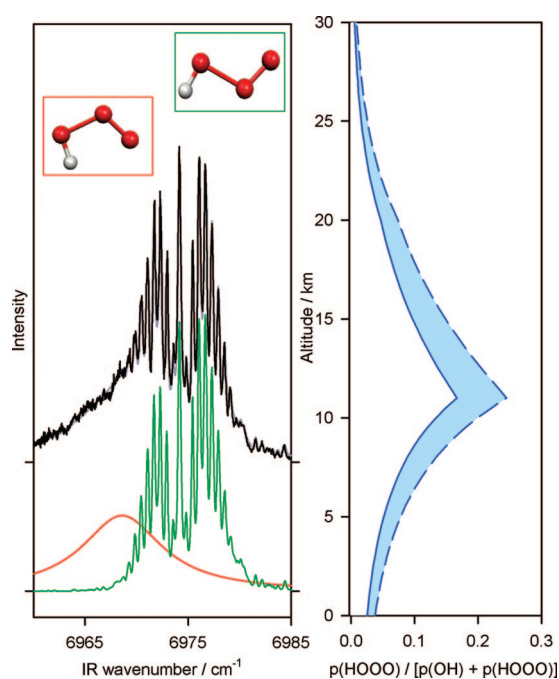
### CON SPECTUS

**W**eakly bound molecules—particularly hydrated complexes of abundant atmospheric species—have long been postulated to play an important role in atmospherically relevant reactions. For example, such complexes could seed cloud formation and alter the global radiation budget. In this Account, we initially describe the current data on weakly bound species produced in association reactions of the hydroxyl radical (OH) with molecular partners, particularly oxygen ( $O_2$ ), nitric acid ( $HONO_2$ ), and nitrogen dioxide ( $NO_2$ ). Researchers have identified weakly bound association products of these reactions as the hydrogen trioxy (HOOO) radical, the doubly hydrogen-bonded OH– $HONO_2$  complex, and peroxyxynitrous acid ( $HOONO$ ), respectively. In each case, previous kinetic studies of the reaction or OH vibrational relaxation processes have indicated unusual, non-Arrhenius behavior. Under the temperature–pressure conditions of the Earth’s lower atmosphere, these processes exhibit a negative temperature dependence, indicative of an attractive interaction, or a pressure dependence. Researchers have subsequently carried out extensive theoretical studies of the properties of these weakly bound molecules, but the theoretical studies have lacked experimental validation.

Next, we describe experimental studies to determine the vibrational frequencies and stability of HOOO as a prototypical example of these weakly bound molecules. We then use these data to assess its importance in the atmosphere.

We discuss the efficient production of the HOOO radical from OH and  $O_2$  under laboratory conditions and its subsequent detection using infrared action spectroscopy, a highly sensitive and selective double resonance technique. Using excitation of OH stretch and combination bands comprising OH stretch with lower frequency modes, we obtain detailed spectroscopic information on the vibrational modes of the two conformers of HOOO. In addition, we infer fundamental information about the dissociation dynamics from the OH product state distribution, which provides insight into the chemical bonding in HOOO. Perhaps most importantly, we utilize a simple conservation of energy relationship based on the highest energetically open OH product state to derive a rigorous upper limit for the stability of HOOO relative to the OH +  $O_2$  asymptote of  $5.3 \text{ kcal mol}^{-1}$ .

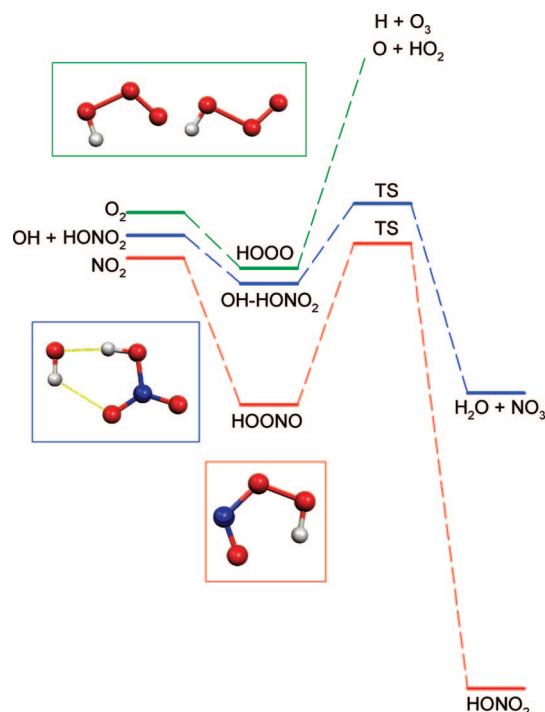
When combined with previous experimental rotational constants that reflect the structure of the HOOO radical, our laboratory characterization of its stability and vibrational frequencies provides critical information to assess its thermochemical properties. Using standard statistical mechanics approaches, we can calculate the likely atmospheric abundance of HOOO. We estimate that up to 25% of the OH radicals in the vicinity of the tropopause may be associated with  $O_2$  as a weakly bound molecule.



## Introduction

The precise role played in atmospheric chemistry by weakly bound species is uncertain. Several authors have speculated that weakly bound complexes composed of abundant atmospheric species, and in particular hydrated complexes, could have an impact for a variety of reasons given in representative literature.<sup>1–3</sup> To date, however, only the  $O_2-O_2$  collision complex<sup>4–6</sup> has been directly detected in the atmosphere, although there have also been several attempts to observe the water dimer.<sup>4,7,8</sup> Initial formation of complexes could provide seeds for the growth of larger aerosols, enhancing cloud formation. The vibrational frequencies of X–H stretches in hydrogen-bonded species typically display large red shifts in conjunction with order of magnitude enhancements in intensity and thus are moved away from the free monomer absorptions. If present in concentrations that approach the monomers, this could directly affect global radiation budgets. Complexes may also present photochemistry and reactivity that differ from monomers. For example, the formation of a complex between water and acetaldehyde has been demonstrated to lower the energy of the transition state for hydrogen abstraction by hydroxyl radicals, providing an example of a chaperone mechanism, in which the complex is more reactive than the monomer.<sup>9</sup>

How stable must a weakly bound molecule be to exist in sufficient concentration under the typical temperature and pressure conditions of the atmosphere or, alternatively, participate as an intermediate in an important atmospheric reaction? We focus on molecules with dissociation energies,  $D_0$ , ranging from a few to a few tens of kilocalories per mole. These species are therefore significantly more strongly bound than  $kT$  ( $0.6 \text{ kcal mol}^{-1}$  at room temperature) and more stable than van der Waals complexes, which typically have  $D_0 \leq 1 \text{ kcal mol}^{-1}$ . Examples include dimers involving radical species that may form reactive intermediates, complexes with atmospheric water, or less stable isomers of relatively common atmospheric molecules. In addition to  $D_0$ , which dominates the enthalpy change of forming the weakly bound molecule, the likely concentration of a given weakly bound molecule in the atmosphere is also strongly influenced by the entropy.<sup>10</sup> Reliable estimates of likely concentrations derived from statistical mechanical considerations therefore require accurate knowledge of not only binding energies but also spectroscopic properties, such as rotational constants and vibrational frequencies. While such properties are in principle obtainable from theory, our case study of the hydrogen tri-oxo (HOOO) radical will demonstrate that this is not always



**FIGURE 1.** Schematic of stationary points along the reaction coordinates for OH with  $O_2$ ,  $HONO_2$ , and  $NO_2$  illustrating the weakly bound molecules that play a role in these reactions under atmospheric conditions. The structures of HOOO, OH-HONO<sub>2</sub>, and HONO<sub>2</sub> are shown in color-coded boxes along with their approximate stabilities relative to reactant and product asymptotes. The OH + HONO<sub>2</sub> reaction and HONO<sub>2</sub> isomerization proceed over small barriers (labeled TS to indicate the transition state) to products.

straightforward and that high-quality fundamental laboratory studies are highly desirable, if not essential.

This Account focuses on weakly bound species produced in association reactions of the hydroxyl radical (OH) with molecular partners. By way of an introduction, we present two examples: (1) the doubly H-bonded OH–HONO<sub>2</sub> complex and (2) peroxyxynitrous acid (HOOONO), an isomer of nitric acid (HONO<sub>2</sub>). Both species are involved in the HO<sub>x</sub> and NO<sub>x</sub> cycles, for which HONO<sub>2</sub> is an atmospheric reservoir species, and both are stable by less than  $20 \text{ kcal mol}^{-1}$ . Schematic reaction profiles are shown in Figure 1. In the lower troposphere, HONO<sub>2</sub> is photochemically stable and has a long lifetime (ca. 120 days) with respect to reaction with OH radicals; consequently, it is primarily removed by dry deposition and rainout.<sup>11</sup> However, at higher altitudes, solar photolysis and reaction with OH radicals provide competitive removal pathways and regenerate reactive NO<sub>x</sub>. Kinetic studies have shown unusual temperature and pressure dependences and a pronounced kinetic isotope effect.<sup>12</sup> The proposed mechanism for the OH + HONO<sub>2</sub> reaction involves the production of an energized intermediate, which can be collisionally stabilized, dis-

sociate back to products, or tunnel through a barrier to products. The important role played by weakly bound reactive intermediates in the kinetics of reactions involving OH radicals was discussed in detail by Smith and Ravishankara.<sup>13</sup>

O'Donnell et al.<sup>14</sup> have recently prepared the OH–HONO<sub>2</sub> intermediate in a supersonic free-jet expansion and identified the radical and acid OH stretch fundamental bands as well as their fully deuterated analogs. The observed frequency shifts from the equivalent monomer bands were consistent with theoretical predictions based upon a doubly H-bonded cyclic structure. The primary H-bonding interaction occurs between the acidic proton and the O atom of the radical, leading to a large red shift of  $-290\text{ cm}^{-1}$  relative to the acid OH stretching frequency. The weaker H-bonding interaction in which the OH radical acts as the donor gives rise to a smaller red shift of  $-52\text{ cm}^{-1}$ . Analysis of the nascent distribution of OH product states following vibrational predissociation of the excited OH–HONO<sub>2</sub> complex led to an upper limit for  $D_0$  of  $5.3\text{ kcal mol}^{-1}$ , which is in good accord with theoretical predictions. These results provided definitive spectroscopic identification of the complex postulated to play a key role in the kinetics of the OH + HONO<sub>2</sub> reaction.<sup>12,13</sup>

Nitric acid itself is produced in the atmosphere as the primary product of the three-body association of OH and NO<sub>2</sub>. However, measurements of the temperature and pressure dependence of this reaction led to suggestions that a small but significant fraction may reversibly form the less stable HOONO isomer.<sup>15</sup> HOONO has two stable conformational minima, labeled by the torsion angle about the OONO and HOON moieties: *cis–cis* is stable by  $\sim 19.8\text{ kcal mol}^{-1}$  and *trans–perp* by  $16.2\text{ kcal mol}^{-1}$ .<sup>16,17</sup> The work in this laboratory used jet-cooled action spectroscopy to identify the OH stretch overtone<sup>17</sup> and second overtone<sup>18</sup> transitions of *trans–perp*-HOONO.

The *cis–cis* conformer has been detected under thermal flow cell conditions.<sup>16,19</sup> Its action spectrum in the OH overtone region is skewed in appearance with lower energy features (including the band origin) suppressed relative to hot bands originating from excited torsional levels that have sufficient energy to dissociate.<sup>20</sup> The *cis–cis* conformer has also been characterized by cavity ring-down absorption and pure rotational spectroscopy.<sup>21,22</sup> Master equation modeling based on spectroscopic parameters and binding energies indicates that the fractional yield of HOONO relative to HONO<sub>2</sub> in the atmosphere may be as high as 20% in the vicinity of the tropopause.<sup>15</sup>

In the remainder of this Account, we present a case study focusing on our recent work on HOOO, a weakly bound mol-

ecule formed by the three-body association reaction between hydroxyl and molecular oxygen, which is also a transient intermediate in several important atmospheric reactions. Laboratory characterization of HOOO provides invaluable measurements of its stability relative to the OH + O<sub>2</sub> asymptote, as well as its vibrational frequencies, which are essential for estimating likely atmospheric abundance using standard statistical mechanics approaches. Furthermore, from a fundamental perspective, study of the vibrational predissociation dynamics has provided insight into the nature of the chemical bonding in this exotic trioxy species, which has proven to be a challenging case for electronic structure theory.

## A Case Study: The Hydrotrioxy (HOOO) Radical

Our main interest in HOOO is the role that it plays as a transient intermediate in several important reactions in the upper atmosphere and the possibility that it may act as a temporary sink for reactive OH radicals at lower altitudes. The highly exothermic atom–molecule reaction  $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$  is involved in the destruction of odd-oxygen species in the upper troposphere and mesosphere. While a simple H-atom abstraction mechanism may have been anticipated, elegant kinetic studies<sup>23</sup> using isotopically labeled <sup>18</sup>O reagents have demonstrated conclusively that the HOOO minimum is sampled as the reaction proceeds quantitatively to <sup>16</sup>OH + <sup>18</sup>O<sup>16</sup>O. Also in the mesosphere, the reaction  $\text{H} + \text{O}_3$  is responsible for the Meinel bands of OH in the atmospheric airglow.<sup>11</sup> The highly vibrationally excited OH products,  $\nu \leq 9$ , emit on strong fundamental and weaker overtone vibration–rotation transitions and stretch from the mid-IR to the ultraviolet. Nonradiative relaxation of the highly inverted nascent vibrational distribution is caused by collisions with atmospheric constituent gases, of which O<sub>2</sub> is by far the most important. The efficiency and negative temperature dependence of the kinetics of collisional vibrational relaxation of OH by O<sub>2</sub> indicates an attractive interaction and suggests a HOOO intermediate.<sup>24</sup>

While the implications for HOOO as an important intermediate in atmospheric chemistry are potentially profound, experimental evidence of this radical species remained elusive until recently. The first direct experimental observation of HOOO was in 1999, when Cacace et al.<sup>25</sup> detected HOOO using neutralization–reionization/collisionally activated dissociation mass spectrometry, in which protonated ozone (HO<sub>3</sub><sup>+</sup>) was the precursor. This study confirmed the existence of HOOO and revealed that the lifetime of the neutral species was at least on the order of microseconds. An indirect measurement of the stability of HOOO was made by Sper-

anza,<sup>26</sup> in which the electron transfer efficiency between HO<sub>3</sub><sup>+</sup> and a series of neutrals inferred an enthalpy of formation of HOOO of  $\Delta_f H_{298\text{K}} = -1 \pm 5 \text{ kcal mol}^{-1}$  and consequently a dissociation enthalpy of  $10 \pm 5 \text{ kcal mol}^{-1}$ . The large uncertainty associated with this measurement suggested a need for refinement of the stability of HOOO.

Vibrational transitions attributed to HOOO in Ar matrix have been reported by Nelander et al.<sup>27</sup> Suma et al. recorded pure rotational spectra of HOOO (and DOOO) using Fourier transform microwave (FTMW) spectroscopy.<sup>28</sup> The molecular constants, as well as the ratio of *a*-type and *b*-type transition intensities, were consistent with a *trans* planar structure of <sup>2</sup>A'' character; no evidence of the *cis* conformer was found. The structure for *trans*-HOOO was determined from the *A* and *B* rotational constants with the terminal OH and O<sub>2</sub> bond lengths fixed at *ab initio* values and revealed a relatively long central O–O bond length of 1.688 Å.

Various theoretical approaches have been used to tackle HOOO.<sup>29–31</sup> However, the predicted molecular properties, including geometry, energy, and vibrational frequencies, are strongly dependent on method and basis set and show varying degrees of deviation from measured values. Single reference methods typically give structures with central O–O bonds shorter (by up to 0.3 Å) than was derived from the experimental rotational constants. However, zero-point motion requires care be taken in comparing experimental with calculated structures, especially for molecules demonstrating large amplitude motion.<sup>31</sup> While it has been argued that multireference methods are needed to correctly describe the electronic structure of HOOO, the results of such methods are dependent on the choice of active space, and configuration interaction ought to be accounted for by coupled-cluster calculations with sufficient excitations.

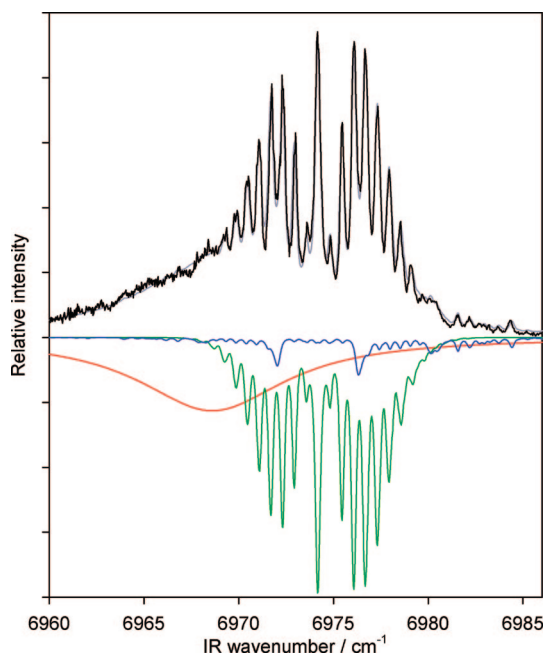
In our laboratory,<sup>32–35</sup> the HOOO radical was prepared in a supersonic free-jet expansion, an experimental technique with a long history in spectroscopy. HONO<sub>2</sub> vapor is seeded in a carrier gas containing a low concentration of a molecular partner (O<sub>2</sub> in Ar) at a (relatively) high stagnation pressure and is allowed to expand through an aperture into a region of much lower pressure. HONO<sub>2</sub> is photolyzed immediately after the nozzle orifice with 193 nm light from an excimer laser to generate OH radicals. The ensuing adiabatic expansion, which results in conversion of the excess energy from photolysis and random thermal motion into unidirectional flow along the expansion axis, provides two principal advantages for infrared action spectroscopy: rotational cooling, which greatly simplifies the observed spectra by limiting population to only the lowest quantum states, and background

reduction discussed below. Under relatively modest expansion conditions, cooling down to a few kelvins is routinely achievable.

The cooling achieved in supersonic free jets has one other significant consequence, the enhanced production of adducts that are moderately stable under atmospheric conditions. Association reactions require three-body collisions, which are enhanced by higher stagnation pressures. The frequency of three-body collisions decreases more rapidly than two-body collisions with increasing distance from the expansion orifice; therefore, it is important for the production of adducts involving radical species that they are generated as early as possible in the expansion.

HOOO radicals were probed using infrared action spectroscopy, an IR-UV double-resonance technique, which provides both high sensitivity and high species selectivity. The concept is straightforward: a UV probe laser is fixed on a selected spectroscopic transition of the OH radical, typically a rovibronic and fine-structure resolved transition of the A–X band, and the resulting laser-induced fluorescence (LIF) is monitored with a photomultiplier tube. An IR pump laser beam, spatially overlapped but temporally preceding the UV probe beam, is scanned in frequency, and the LIF signal is enhanced relative to any background signal; that is, there is action if the IR photon is absorbed by a species that can subsequently predissociate to produce OH radicals in the specific quantum state probed. This affords selectivity for species that are both bound by less than the energy of the IR photon and contain the species probed. A significant advantage over traditional direct absorption or cavity ring-down spectroscopy measurements in the near- or mid-IR is that the spectra are free from congestion from other absorbers in the spectral region under investigation. Once vibrational transitions have been identified, the IR laser can be fixed in frequency and the UV laser scanned to measure the population distribution of the nascent OH products of the vibrational predissociation process.

The IR spectral region in the vicinity of the OH overtone band ( $2\nu_1$ ) at  $\sim 1.4 \mu\text{m}$  was initially surveyed,<sup>32</sup> while the UV laser was used to probe nascent OH  $v = 1$  products of vibrational predissociation. This minimized background signal from residual OH in the expansion since the vibrationally excited level contains a significantly smaller fraction of OH population than  $v = 0$ . Later, we demonstrated that rotational cooling of background OH in  $v = 0$  was sufficient to record infrared action spectra of HOOO in the fundamental OH stretch ( $\nu_1$ ) region with the UV laser probing nascent OH  $v = 0$  products of vibrational predissociation.<sup>33</sup>



**FIGURE 2.** IR action spectrum of the  $2\nu_1$  band of the HOOO radical (black) and overlapping simulation (gray). The individual components of the simulation are shown inverted and comprise the dominant *a*-type (green) and minor *b*-type (blue) contributions of the *trans*-HOOO conformer and the unstructured feature assigned to *cis*-HOOO (red).

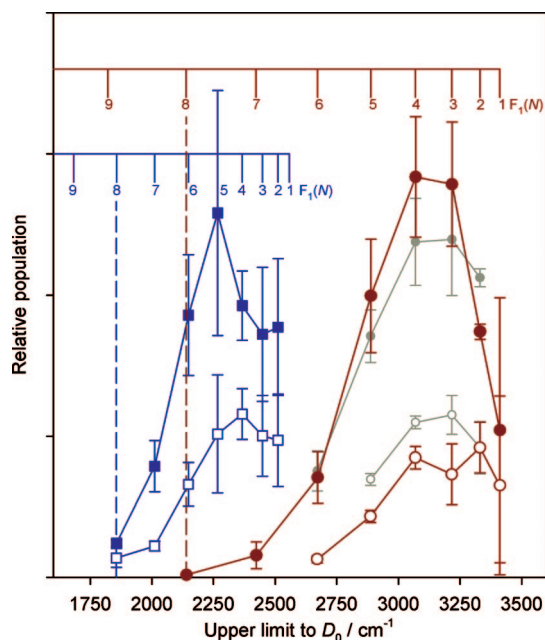
As an example, the jet-cooled ( $\sim 7$  K) overtone spectrum of HOOO is displayed in Figure 2. The spectrum clearly contains two components: a partially rotationally structured band lying at higher frequency and an unstructured band of similar breadth lying at lower frequency. The origins of both bands are shifted only a few  $\text{cm}^{-1}$  from that of the free OH overtone. The structured band could be definitively assigned to *trans*-HOOO on the basis of the excellent agreement with simulations<sup>36</sup> using molecular constants obtained from FTMW work.<sup>28</sup> The rotational contour indicates predominantly *a*-type selection rules and hence a transition dipole moment that is rotated significantly away from the OH bond axis. This provides evidence that the electronic structure on the remainder of the molecule is perturbed upon OH stretch excitation and suggests that there is a chemical interaction between the OH and O<sub>2</sub> moieties.

Assignment of the unstructured feature was obviously more problematic, but several pieces of circumstantial evidence led us to assign it to *cis*-HOOO.<sup>33</sup> First, analogous features were observed adjacent to the OH stretch fundamental of *trans*-HOOO and the OD stretch fundamental and overtone of *trans*-DOOO indicating that OH (or OD) stretches were responsible for the absorption. In all four spectral regions, the unstructured feature was of comparable width ( $\sim 7$   $\text{cm}^{-1}$ ) to the rotationally structured *trans* bands, suggesting that the absorbing

species has similar rotational constants, consistent with it being the *cis* conformer. However, it remains uncertain why this conformer would lack rotational structure, which presumably reflects subpicosecond dynamics in the excited vibrational state. The nearly equal integrated intensities of the unstructured to structured features were furthermore effectively independent of attempts to alter the temperature of the expansion, such as probing further upstream and using He as the carrier gas rather than Ar, excluding the possibility of hot bands or HOOO–Ar clusters. Finally, the nascent OH product state distributions, which will be discussed later, were remarkably similar to those obtained following vibrational predissociation of *trans*-HOOO.

A primary motivation for investigation of HOOO using action spectroscopy was the desire to determine its stability. An upper limit to  $D_0$  can be obtained directly from the measured nascent OH product state distribution following predissociation of the vibrationally excited HOOO radicals and a simple application of conservation of energy. The total energy available after vibrational excitation is the sum of the IR photon energy and the internal energy of the HOOO, the latter being typically only a few wavenumbers on account of the extensive cooling in the expansion. This energy must overcome  $D_0$  with the excess partitioned into relative translation and the internal degrees of freedom of the OH and O<sub>2</sub> products. Measuring the energetically highest open OH product channel (vibration, rotation, and fine-structure) therefore provides a rigorous upper limit to  $D_0$ . An upper limit is obtained because the experiment provides no information on the energy partitioning into O<sub>2</sub> internal excitation or kinetic energy, although both of these quantities are anticipated to be relatively small.<sup>37</sup>

Overtone excited *trans*-HOOO predissociates to OH  $v = 1$  products exclusively, with the distribution over rotational and fine-structure levels shown in Figure 3. The products are most likely to be found in  $N = 4$ , are statistically distributed over the F<sub>1</sub> and F<sub>2</sub> spin–orbit manifolds, and display a strong propensity for  $\Pi(A')$   $\Lambda$ -doublets; that is, the unpaired electron resides in a  $p\pi$  orbital localized in the plane of OH nuclear rotation. The  $\Lambda$ -doublet propensity has been interpreted as indicating planar dissociation of *trans*-HOOO, based on electronic symmetry arguments, and as evidence for a covalent (although weak)  $p\sigma$  bond between the half-filled  $p\pi$  orbital of OH and a half-filled  $\pi^*$  orbital of O<sub>2</sub>.<sup>33</sup> The propensity for  $\Pi(A')$   $\Lambda$ -doublets is marginally reduced following excitation of the *cis*-HOOO feature as shown in Figure 3. The term energy of the highest open channel ( $v = 1$ , F<sub>1</sub>,  $N = 8$ , *e*) following  $2\nu_1$  excitation of *trans*-HOOO directly provides an upper limit to



**FIGURE 3.** Nascent OH (red) and OD (blue)  $X\ 2\Pi_{3/2}, v = 1$  product state distributions arising from vibrational predissociation of *trans*-HOOO and DOOO excited to  $2\nu_1$ . Filled and open symbols are used for  $\Pi(A)$  and  $\Pi(A')$   $\Lambda$ -doublet levels, respectively. The distributions are plotted against the upper limit to  $D_0$ , given by  $h\nu_{\text{IR}} + E_{\text{int}}(\text{H/DOOO}) - E_{\text{int}}(\text{OH/D})$ , with internal energy,  $E_{\text{int}}$ ; *trans*-HOOO was excited at  $6977\text{ cm}^{-1}$ , *cis*-HOOO at  $6965\text{ cm}^{-1}$ , and *trans*-DOOO at  $5185\text{ cm}^{-1}$ . Dashed vertical lines indicate the energetically highest open channel. Also shown is the OH  $X\ 2\Pi_{3/2}, v = 1$  product state distribution obtained following excitation of *cis*-HOOO at  $6965\text{ cm}^{-1}$  (gray).

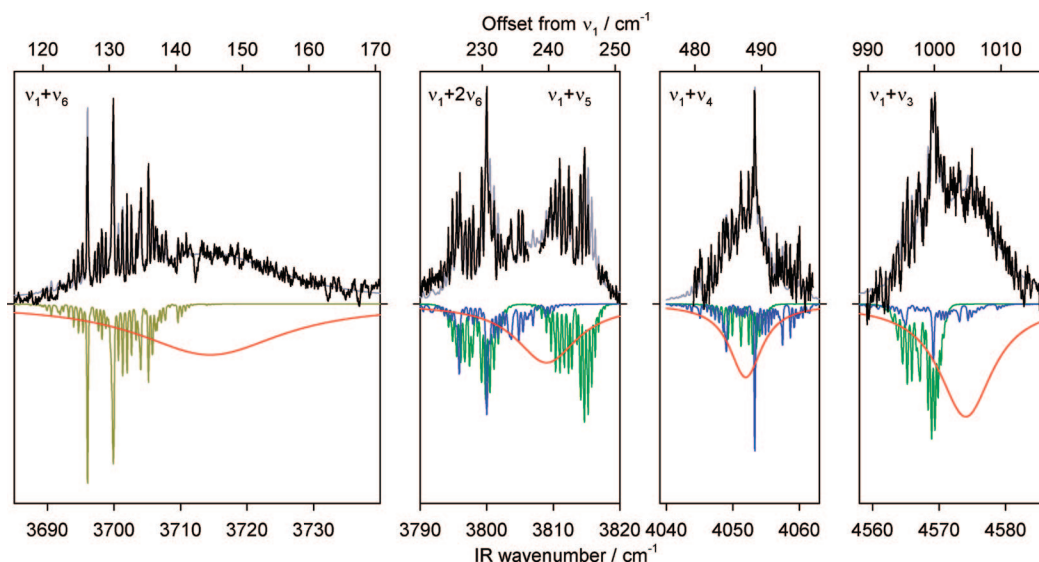
the dissociation energy of  $D_0 \leq 2140\text{ cm}^{-1}$  ( $6.12\text{ kcal mol}^{-1}$ ), as indicated with a red dashed line in Figure 3. However, the fineness of the measurement is inherently limited by the rotational spacing in the OH products; the subsequent favored  $\Pi(A')$  level in the  $F_1$  spin-orbit manifold lies some  $\sim 320\text{ cm}^{-1}$  higher in energy.

In fact, the tightest constraint on  $D_0$  for HOOO is derived from the OD product state distribution obtained following  $2\nu_1$  excitation of *trans*-DOOO,<sup>35</sup> because the rotational spacing is smaller for OD than OH. The OD  $v = 1$  product state distribution stretches as far as the  $F_1, N = 8, f$  level, giving  $D_0 \leq 1860\text{ cm}^{-1}$  ( $5.32\text{ kcal mol}^{-1}$ ), as indicated by the blue dashed line in Figure 3. However, within the Born–Oppenheimer approximation, it is  $D_e$ , rather than  $D_0$ , that is constant for the protiated and deuterated species, and differences in the zero-point energies must be considered. Further refinement of  $D_0$  therefore requires knowledge of the zero-point energies, which for polyatomic molecules also requires all other frequencies and the anharmonic cross-terms be known. In these circumstances, it is common to rely upon *ab initio* predictions; however, this is fraught with difficulty for HOOO. Qualitatively, we antici-

pate that  $D_0$  will be smaller for *trans*-HOOO than for *trans*-DOOO since three vibrational modes are expected to shift to lower frequency upon deuteration, namely, the torsion ( $\nu_6$ ), the HOO bend ( $\nu_3$ ), and the OH stretch ( $\nu_1$ ). Consequently, the upper limit  $D_0$  obtained for *trans*-DOOO is equally applicable to *trans*-HOOO, and the difference will depend predominantly on the shifts of  $\nu_3$  and  $\nu_6$  since  $\nu_1$  in HOOO exhibits a very similar isotope shift to free OH.

The vibrational spectroscopy of HOOO was investigated further<sup>34</sup> to explore the low frequency modes, because knowledge of vibrational frequencies is necessary for an accurate zero-point energy assessment as well as calculation of thermochemical properties of HOOO. Direct excitation of the low-frequency fundamentals is not possible for two reasons. The first is strictly technical, since the optical parametric oscillator used to generate the IR radiation does not operate at the required frequencies, while the second is a consequence of action spectroscopy: excitation of low-frequency modes does not provide sufficient energy to cause vibrational predissociation. Consequently, a broad spectroscopic search was carried out for combination bands ( $\nu_1 + \nu_n$ ) comprising one quantum of OH stretch ( $\nu_1$ ) and one quantum of a lower frequency mode ( $\nu_n$  where  $n = 2-6$ ). Several vibrational features consisting of structured and unstructured components were observed, as displayed in Figure 4. The rotationally structured bands are assigned to combination bands of the *trans* conformer, based on arguments that have been discussed in depth previously.<sup>33,34</sup> The unstructured spectral features were assigned to the analogous  $\nu_1 + \nu_n$  combination bands of the *cis* conformers. That the unstructured *cis* bands are observed adjacent to structured *trans* bands indicates that the vibrational frequencies are not significantly different for the two conformers.

The isotopically substituted DOOO radical aided in definitive assignment of these vibrational bands. In total, five additional bands of HOOO and four of DOOO have been recorded. In each case, the vibrational band origins were derived from a least-squares contour fit to the spectra; the  $\nu_1$  frequency was subtracted from the band origins to obtain approximate fundamental frequencies of the  $\nu_n$  modes. The deviations from the true fundamental frequencies will depend on the magnitudes of cross anharmonicity terms and are expected to be small. Assignments were based on observed vibrational frequencies and isotopic shifts (if present) upon deuteration. In the case of rotationally structured bands, the direction of the transition dipole moment, as evidenced in the intensity ratios of *a*-type (parallel), *b*-type (perpendicular, in-plane), and *c*-type (perpendicular, out-of-plane) transitions, provided further evi-



**FIGURE 4.** IR action spectra of combination bands of HOOO (black) and simulations (gray). Individual components of the simulation are shown inverted and comprise *a*-type (green), *b*-type (blue), and, in the  $\nu_1 + \nu_6$  band, *c*-type (yellow) components of the *trans*-HOOO conformer and unstructured components attributed to combination bands of *cis*-HOOO (red).

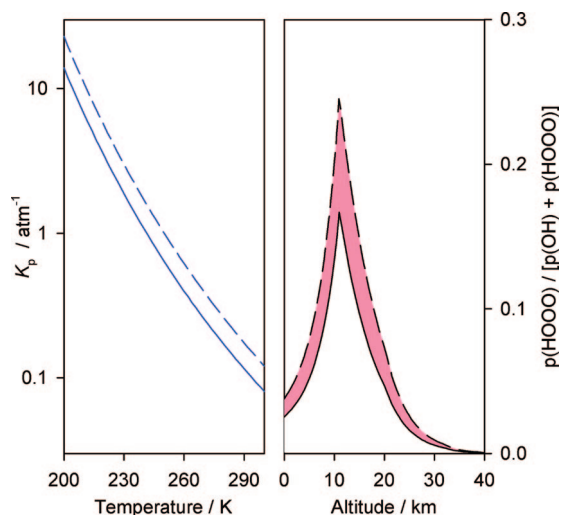
dence for the assignments, and simulations of the individual rotational bands are included in Figure 4.

The lowest frequency  $\nu_1 + \nu_n$  combination band of *trans*-HOOO was observed at  $+128.7 \text{ cm}^{-1}$  relative to  $\nu_1$  and exhibits exclusively *c*-type rotational band structure. An analogous *trans*-DOOO band was observed at  $+102.2 \text{ cm}^{-1}$ . The isotope shift of  $\sim 26 \text{ cm}^{-1}$  is consistent with vibrational motion involving predominantly the light H/D atom, and the band type requires a mode of  $a''$  symmetry. Thus, these bands are attributed to the torsional vibration,  $\nu_6$ . It should be noted that the  $\nu_1 + \nu_6$  band was the most intense combination band ( $\sim 25\%$  of  $\nu_1$ ), while the other bands were all approximately 20 times weaker than the  $\nu_1$  band. For *trans*-HOOO,  $\nu_1 + 2\nu_6$  was also observed at  $+228.7 \text{ cm}^{-1}$  and exhibits *a/b*-type hybrid rotational structure as would be expected for an even quantum change in the asymmetric mode. Two additional bands were observed for *trans*-HOOO with offsets of  $+243.7 \text{ cm}^{-1}$  and  $+481.9 \text{ cm}^{-1}$ . Assignment of these bands was facilitated by comparison with bands of *trans*-DOOO at  $+245.3$  and  $+463 \text{ cm}^{-1}$  that showed analogous transition types and only very small isotope shifts indicating the vibration involved heavy atom motion. As such, the frequency ordering allowed these bands to be assigned to combination bands involving the central OO stretch,  $\nu_5$ , and the OOO bend,  $\nu_4$ . The highest frequency combination bands were observed at  $+997.9 \text{ cm}^{-1}$  for *trans*-HOOO and  $+783.9 \text{ cm}^{-1}$  for *trans*-DOOO and were attributed to H/DOO bend,  $\nu_3$ , consistent with the significant isotopic shift.

These data represented the first gas-phase observation of the low-frequency modes of HOOO and DOOO and were

found to differ significantly from theoretical predictions. This discrepancy is likely a consequence of the calculated geometry and manifests itself throughout all properties of the central OO bond; somewhat paradoxically, experiments reveal a longer, stronger bond with lower vibrational frequency than theoretical predictions.

Finally, with experimentally determined quantities, namely,  $D_0 \leq 1856 \text{ cm}^{-1}$ ,<sup>35</sup> the rotational constants from the FTMW study<sup>28</sup> and the vibrational frequencies derived from combination bands,<sup>34</sup> standard statistical mechanics calculations were employed to estimate the equilibrium constant,  $K_p(T)$ , for the  $\text{OH} + \text{O}_2 + \text{M} \rightleftharpoons \text{HOOO} + \text{M}$  association reaction (with collision partner M) and subsequently the atmospheric abundance of HOOO. In the present treatment,  $K_p(T)$  was calculated within the rigid-rotor harmonic oscillator approximation, which has known limitations for weakly bound species at atmospheric temperatures. While more sophisticated treatments of calculating partition functions of dimers have been reported,<sup>38–40</sup> the present analysis provides a reasonable estimate given the residual uncertainties. The torsional mode presents an additional problem, since the barrier for *trans*–*cis* isomerization is essentially unknown. A useful range of  $K_p$  can be calculated by treating  $\nu_6$  as either a harmonic oscillator, in common with the other modes, for *trans* and *cis* HOOO or a free rotor. The magnitude of  $K_p$  increases with decreasing temperature, favoring the production of HOOO at low temperatures as shown in Figure 5. Consideration of both the temperature and pressure profile in the Earth's atmosphere reveals that the fraction of OH expected to be associated with  $\text{O}_2$  as HOOO,  $p(\text{HOOO})/[p(\text{OH}) + p(\text{HOOO})]$ , expressed in



**FIGURE 5.** The temperature dependence (left panel) of  $K_p$  for the equilibrium reaction  $\text{OH} + \text{O}_2 + \text{M} \rightleftharpoons \text{HOOO} + \text{M}$  is estimated treating the lowest frequency torsional mode in the harmonic oscillator (solid line) and free rotor (dashed line) limits. The formation of HOOO is favored at temperatures below  $\sim 245$  K. The temperature and pressure profiles (right panel) of the atmosphere are incorporated to obtain the HOOO abundance as a fraction of hydroxyl concentration,  $p(\text{HOOO})/[p(\text{OH}) + p(\text{HOOO})]$ , which reaches a maximum at an altitude of  $\sim 11$  km in the tropopause region of the atmosphere.

terms of partial pressures, is largest at the tropopause ( $\sim 11$  km) and decreases at both lower and higher altitudes as a consequence of increasing temperature and decreasing pressure, respectively, as shown in Figure 5. These calculations indicate that up to 25% of the OH radicals in the vicinity of the tropopause may be associated with  $\text{O}_2$  as weakly bound HOOO radicals.

These experimental results are particularly relevant to possible detection of HOOO in the atmosphere, where low-frequency vibrations (or microwave transitions) are preferable for both *in situ* and remote sensing methods. Atmospheric detection also requires a clear spectral window where there is no strong atmospheric absorber, for example,  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . The HOOO torsion at  $129\text{ cm}^{-1}$  and OOO bend at  $482\text{ cm}^{-1}$  are therefore plausible targets for field measurements using Fourier-transform emission, which has been used for the detection of trace species such as OH in the stratosphere. Recent advances in the capabilities of airborne spectrometers have made it possible to extend these measurements into the upper troposphere and lower stratosphere.<sup>41</sup>

## Conclusions

We have presented a summary of our recent studies of the HOOO radical, an important transient intermediate in the atmosphere. We have obtained detailed spectroscopic infor-

mation including vibrational frequencies via fundamental excitation of OH stretch and in combination bands, as well as information on the vibrational predissociation dynamics of HOOO and elucidation of the stereochemical signature of the dissociation. Perhaps most important is the determination of a rigorous upper limit to the stability of HOOO relative to  $\text{OH} + \text{O}_2$ . Taken together with experimental rotational constants, this data set contains the necessary information for statistical mechanical calculations of the equilibrium and subsequent assessment of the atmospheric abundance of HOOO, as reported here, suggesting that HOOO is a potentially significant sink for OH radicals.

Of course, additional aspects of HOOO chemistry will influence its importance in the atmosphere and warrant further research. These include investigation of the photochemistry of electronic absorption to dissociative states in the ultraviolet or visible wavelength regions, which may be important in the presence of sunlight under atmospheric conditions. Additionally, understanding of the reactivity of HOOO with trace species, specifically in comparison to the reactivity of OH radicals, is needed.

This Account illustrates the importance of laboratory measurements of fundamental spectroscopic and dynamical information in providing critical information necessary to assess thermochemical properties and evaluate the atmospheric importance of the HOOO radical and other weakly bound molecules.

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## FOOTNOTES

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## REFERENCES

- Kjaergaard, H. G.; Robinson, T. W.; Howard, D. L.; Daniel, J. S.; Headrick, J. E.; Vaida, V. Complexes of importance to the absorption of solar radiation. *J. Phys. Chem. A* **2003**, *107*, 10680–10686.
- Vaida, V.; Kjaergaard, H. G.; Feierabend, K. J. Hydrated complexes: Relevance to atmospheric chemistry and climate. *Int. Rev. Phys. Chem.* **2003**, *22*, 203–203.
- Aloisio, S.; Francisco, J. S. Radical–water complexes in Earth’s atmosphere. *Acc. Chem. Res.* **2000**, *33*, 825–830.
- Solomon, S.; Portmann, R. W.; Sanders, R. W.; Daniel, J. S. Absorption of solar radiation by water vapor, oxygen, and related collision pairs in the Earth’s atmosphere. *J. Geophys. Res., [Atmos.]* **1998**, *103*, 3847–3858.
- Pfeilsticker, K.; Erle, F.; Platt, U. Absorption of solar radiation by atmospheric O<sub>4</sub>. *J. Atmos. Sci.* **1997**, *54*, 933–939.
- Pfeilsticker, K.; Bösch, H.; Camy-Peyret, C.; Fitzenberger, R.; Harder, H.; Osterkamp, H. First atmospheric profile measurements of UV/visible O<sub>4</sub> absorption band intensities: Implications for the spectroscopy, and the formation enthalpy of the O<sub>2</sub>–O<sub>2</sub> dimer. *Geophys. Res. Lett.* **2001**, *28*, 4595–4598.
- Pfeilsticker, K.; Lotter, A.; Peters, C.; Bosch, H. Atmospheric detection of water dimers via near-infrared absorption. *Science* **2003**, *300*, 2078–2080.
- Ptashnik, I. V. Evidence for the contribution of water dimers to the near-IR water vapour self-continuum. *J. Quant. Spectrosc. Radiat. Transfer* **2008**, *109*, 831–852.
- Vöhringer-Martinez, E.; Hansmann, B.; Hernandez, H.; Francisco, J. S.; Troe, J.; Abel, B. Water catalysis of a radical-molecule gas-phase reaction. *Science* **2007**, *315*, 497–501.
- Vaida, V.; Headrick, J. E. Physicochemical properties of hydrated complexes in the Earth’s atmosphere. *J. Phys. Chem. A* **2000**, *104*, 5401–5412.
- Wayne, R. P. *Chemistry of Atmospheres*, 3rd ed.; Oxford University Press: New York, 2000.
- Brown, S. S.; Talukdar, R. K.; Ravishankara, A. R. Reconsideration of the rate constant for the reaction of hydroxyl radicals with nitric acid. *J. Phys. Chem. A* **1999**, *103*, 3031–3037.
- Smith, I. W. M.; Ravishankara, A. R. Role of hydrogen-bonded intermediates in the bimolecular reactions of the hydroxyl radical. *J. Phys. Chem. A* **2002**, *106*, 4798–4807.
- O’Donnell, B. A.; Li, E. X. J.; Lester, M. I.; Francisco, J. S. Spectroscopic identification and stability of the intermediate in the OH + HONO<sub>2</sub> reaction. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12678–12683.
- Golden, D. M.; Barker, J. R.; Lohr, L. L. Master equation models for the pressure- and temperature-dependent reactions HO + NO<sub>2</sub> → HONO<sub>2</sub> and HO + NO<sub>2</sub> → HOONO. *J. Phys. Chem. A* **2003**, *107*, 11057–11071.
- Matthews, J.; Sinha, A. State-resolved unimolecular dissociation of cis-cis HOONO: Product state distributions and action spectrum in the 2ν<sub>OH</sub> band region. *J. Chem. Phys.* **2005**, *122*, 104313.
- Konen, I. M.; Pollack, I. B.; Li, E. X. J.; Lester, M. I.; Varner, M. E.; Stanton, J. F. Infrared overtone spectroscopy and unimolecular decay dynamics of peroxyxynitrous acid. *J. Chem. Phys.* **2005**, *122*, 094320.
- Konen, I. M.; Li, E. X. J.; Stephenson, T. A.; Lester, M. I. Second OH overtone excitation and statistical dissociation dynamics of peroxyxynitrous acid. *J. Chem. Phys.* **2005**, *123*, 204318.
- Fry, J. L.; Nizkorodov, S. A.; Okumura, M.; Roehl, C. M.; Francisco, J. S.; Wennberg, P. O. Cis-cis and trans-perp HOONO: Action spectroscopy and isomerization kinetics. *J. Chem. Phys.* **2004**, *121*, 1432–1448.
- McCoy, A. B.; Fry, J. L.; Francisco, J. S.; Mollner, A. K.; Okumura, M. Role of OH-stretch/torsion coupling and quantum yield effects in the first OH overtone spectrum of cis-cis HOONO. *J. Chem. Phys.* **2005**, *122*, 104311.
- Bean, B. D.; Mollner, A. K.; Nizkorodov, S. A.; Nair, G.; Okumura, M.; Sander, S. P.; Peterson, K. A.; Francisco, J. S. Cavity ringdown spectroscopy of cis-cis HOONO and the HOONO/HONO<sub>2</sub> branching ratio in the reaction OH + NO<sub>2</sub> + M. *J. Phys. Chem. A* **2003**, *107*, 6974–6985.
- Drouin, B. J.; Fry, J. L.; Miller, C. E. Rotational spectrum of cis-cis HOONO. *J. Chem. Phys.* **2004**, *120*, 5505–5508.
- Sridharan, U. C.; Klein, F. S.; Kaufman, F. Detailed course of the O + HO<sub>2</sub> reaction. *J. Chem. Phys.* **1985**, *82*, 592–593.
- McCabe, D. C.; Smith, I. W. M.; Rajakumar, B.; Ravishankara, A. R. Rate coefficients for the relaxation of OH (ν = 1) by O<sub>2</sub> at temperatures from 204–371 K and by N<sub>2</sub>O from 243–372 K. *Chem. Phys. Lett.* **2006**, *421*, 111–117.
- Cacace, F.; De Petris, G.; Pepi, F.; Troiani, A. Experimental detection of hydrogen trioxide. *Science* **1999**, *285*, 81–82.
- Speranza, M. Structure, stability, and reactivity of cationic hydrogen trioxides and thermochemistry of their neutral analogs. A Fourier-transform ion cyclotron resonance study. *Inorg. Chem.* **1996**, *35*, 6140–6151.
- (a) Nelander, B.; Engdahl, A.; Svensson, T. The HOOO radical. A matrix isolation study. *Chem. Phys. Lett.* **2000**, *332*, 403–408. (b) Erratum *Chem. Phys. Lett.*, **2001**, *339*, 295.
- Suma, K.; Sumiyoshi, Y.; Endo, Y. The rotational spectrum and structure of the HOOO radical. *Science* **2005**, *308*, 1885–1886.
- Fabian, W. M. F.; Kalcher, J.; Janoschek, R. Stationary points on the energy hypersurface of the reaction O<sub>3</sub> + H\* → [\*O<sub>3</sub>H] ↔ O<sub>2</sub> + \*OH and thermodynamics functions of \*O<sub>3</sub>H at G3MP2B3, CCSD(T)-CBS(W1U) and MR-ACPF-CBS levels of theory. *Theor. Chem. Acc.* **2005**, *114*, 182–188.
- Yu, H. G.; Varandas, A. J. C. Ab initio theoretical calculation and potential energy surface for ground-state HO<sub>3</sub>. *Chem. Phys. Lett.* **2001**, *334*, 173–178.
- Varner, M. E.; Harding, M. E.; Gauss, J.; Stanton, J. F. On the geometry of the HO<sub>3</sub> radical. *Chem. Phys.* **2008**, *346*, 53–55.
- Murray, C.; Derro, E. L.; Sechler, T. D.; Lester, M. I. Stability of the hydrogen trioxy radical via infrared action spectroscopy. *J. Phys. Chem. A* **2007**, *111*, 4727–4730.
- Derro, E. L.; Murray, C.; Sechler, T. D.; Lester, M. I. Infrared action spectroscopy and dissociation dynamics of the HOOO radical. *J. Phys. Chem. A* **2007**, *111*, 11592–11601.
- Derro, E. L.; Sechler, T. D.; Murray, C.; Lester, M. I. Observation of ν<sub>1</sub> + ν<sub>n</sub> combination bands of the HOOO and DOOO radicals using infrared action spectroscopy. *J. Chem. Phys.* **2008**, *128*, 244313.
- Derro, E. L.; Sechler, T. D.; Murray, C.; Lester, M. I. Infrared action spectroscopy of the OD stretch fundamental and overtone transitions of the DOOO radical. *J. Phys. Chem. A* **2008**, *112*, 9269–9276.
- PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>.
- The O<sub>2</sub> product is expected to have a similar degree of rotational excitation (up to 8ħ or 100 cm<sup>-1</sup>) as OH. Furthermore, translational energy release in vibrational predissociation of weakly bound species is generally minimized. See, for example: Beswick, J. A.; Jortner, J. Intramolecular dynamics of van der Waals molecules. *Adv. Chem. Phys.* **1981**, *47*, 363–506.
- Goldman, N.; Fellers, R. S.; Leforestier, C.; Saykally, R. J. Water dimers in the atmosphere: Equilibrium constant for water dimerization from the VRT(ASP-W) potential surface. *J. Phys. Chem. A* **2001**, *105*, 515–519.
- Schenter, G. K.; Kathmann, S. M.; Garrett, B. C. Equilibrium constant for water dimerization: Analysis of the partition function for a weakly bound system. *J. Phys. Chem. A* **2002**, *106*, 1557–1566.
- Vigasín, A. A. Water vapor continuous absorption in various mixtures: possible role of weakly bound complexes. *J. Quant. Spectrosc. Radiat. Transfer* **2000**, *64*, 25–40.
- Mlynczak, M. G.; Johnson, D. G.; Latvakoski, H.; Jucks, K.; Watson, M.; Kratz, D. P.; Bingham, G.; Traub, W. A.; Wellard, S. J.; Hyde, C. R.; Liu, X. First light from the far-infrared spectroscopy of the troposphere (FIRST) instrument. *Geophys. Res. Lett.* **2006**, *33*, L07704.