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The H_2O-O_2 water vapour complex in the Earth's atmosphere

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Abstract. Until recently, abundance estimates for bound molecular complexes have been affected by uncertainties of a factor 10–100. This is due to the difficulty of accurately obtaining the equilibrium constant, either from laboratory experiments or by statistical thermodynamic calculations. In this paper, we firstly present laboratory experiments that we performed in order to determine the molecular structure of H_2O-O_2. We also derive global abundance estimates for H_2O-O_2 in the Earth's atmosphere. The equilibrium constant K_p evaluated using the "anharmonic oscillator approach" (AHOA) (Sabu et al., 2005) was employed: the AHOA explains well the structure of the complex obtained by the present experiment. The K_p calculated by this method shows a realistic temperature dependence. We used this K_p to derive global abundance estimates for H_2O-O_2 in the Earth's atmosphere. The distribution of H_2O-O_2 follows that of water vapour in the troposphere and seems inversely proportional to temperature in the lower stratosphere. Preliminary estimates at the surface show amount of H_2O-O_2 is comparable to CO or N_2O, ranking water vapour complexes among the ten most abundant species in the boundary layer.

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1 Introduction

Molecular complexes in the Earth's atmosphere are of two types: collisional, such as the oxygen dimer $O_2{\cdot}O_2$, or bound – van der Waals complexes – like the water vapour dimer H_2O-H_2O. In both cases, we can assume that they are at equilibrium with their parent molecules in the atmosphere. Their formation and loss processes can then be expressed as a reaction of the type [A] + [B] $\rightleftharpoons$ [A−B], with an equilibrium constant usually noted K_p.

Collisional complexes have a short atmospheric lifetime, of the order of a few picoseconds, and a broad spectrum for absorption of solar radiation. They can be observed in the UV/Visible spectral range and have already been measured by satellite-borne instruments. These measurements are often used, for example, to obtain cloud top heights. The abundance of collision complexes depends on the partial pressure of the parent molecules, such as O_2, H_2O or N_2, and on the temperature. Their atmospheric abundance and variations are quite well known.

On the other hand, there have been no reports of unambiguous detection of bound complexes in the atmosphere so far. In the past 2–3 decades, numerous laboratory and theoretical studies of bound complexes have been published (e.g., Calo and Narcisi, 1980; Tao et al., 1996; Paul et al., 1997; Svishchev and Boyd, 1998; Aloisio and Francisco, 2000; Vaida et al., 2001; Headrick and Vaida, 2001; Robinson and Kjaergaard, 2003; Paynter et al., 2009).

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Theoretically, it should be possible to evaluate the atmospheric abundance of bound molecular complexes using the equilibrium constant K_p. But estimating K_p is not a trivial task, either by laboratory experiments or statistical thermodynamic calculations, and both estimations are still affected by large uncertainties. Knowing the molecular structure of the complex is also a major issue in estimating the K_p, since the calculation requires knowledge of the partition function and of the binding energy (Vaida and Headrick, 2000).

Among the bound complexes, water vapour complexes (H_2O-X with, e.g., X = H_2O, O_2 or N_2), are expected to have a combined surface abundance at the ppmv level, as estimated by statistical thermodynamic calculations (for example, Vaida et al., 2001). This represents ten times the amount of CO or N_2O and would place hydrated complexes among the ten most abundant molecular compounds at ground level. More accurate knowledge of the equilibrium constant is thus of primary importance to assess their atmospheric role.

We succeeded in determining the structure of the H_2O-O_2 complex by Fourier-transform microwave (FTMW) spectroscopy in the laboratory. The experimental structure and rotational constant are in good agreement with the theoretical results with the anharmonic oscillator approach (AHOA) by us (Sabu et al., 2005). The equilibrium constant, K_p, evaluated by the AHOA (Sabu et al., 2005) was used to estimate the atmospheric abundance of H_2O-O_2.

2 Determination of the molecular structure of the H_2O-O_2 complex

2.1 Laboratory experiment

We generated and observed the H_2O-O_2 spectrum using a pulsed nozzle (PN) Fourier-transform microwave (FTMW) spectrometer. A detailed description of the PN-FTMW spectrometer used in this study was presented in an earlier report (Ohshima and Endo, 1992). In short, the gas mixture of H_2O and O_2 in a concentration of 0.4 % and 0.2 %, respectively, diluted in Ar was expanded into a Fabry-Perot cavity at a stagnation pressure of 3039 hPa (3 atm) through a solenoid valve and adiabatically cooled to a few Kelvin during supersonic expansion. The pressure was approximately 5×10^{-5} torr inside the chamber. The frequency region of the measurement was from 8 GHz to 30 GHz with a resolution of 4 kHz. The signals were integrated from a hundred to a few thousand pulses to achieve adequate signal-to-noise ratio. We confirmed that the observed transitions belonged to H_2O-O_2 by verifying the following conditions:

1. When a sample without O_2 was used in the gas mixture, the signals disappeared. Similarly, without H_2O in the gas mixture, no spectral signature was observed.

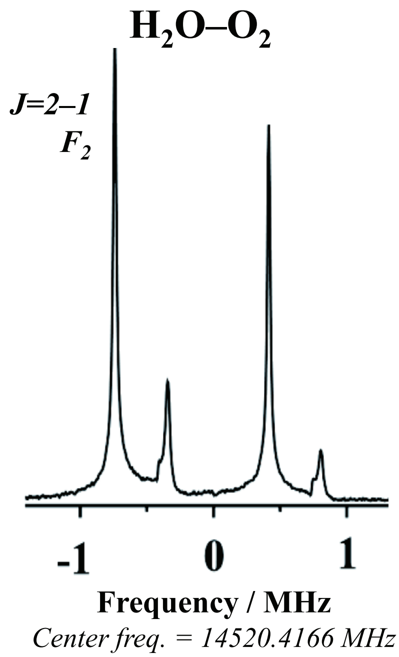

Fig. 1. Example of spectra acquired with the PN-FTMW around 14520.4 MHz, attributed to the van der Waals complex H_2O-O_2.

2. Paramagnetic behavior due to the oxygen molecule. By applying a magnetic field, we confirmed that the lines were due to a paramagnetic species.

3. Magnetic hyperfine structure due to the presence of two non-zero nuclear spins with $I = 1$. The magnetic hyperfine structure was observed with a relatively small (< MHz) splitting in each of the observed rotational transitions. This is considered to be due to water vapour, since $I = 1$ is the composite angular momentum of the two equivalent proton spins in the water molecule. The water molecule has a large amplitude motion with respect to the C_2 axis and the average structure is C_{2v}, as explained in Sabu et al. (2004, 2005).

A total of 21 transitions including fine and hyperfine splittings were successfully observed in the 8–30 GHz region. They are listed in Table 1, which also gives the less numerous D_2O-O_2 observed transitions. An example spectrum for H_2O-O_2 around 14 520 MHz is shown in Fig. 1.

2.2 Spectral analysis

We succeeded in analyzing the spectrum of the H_2O-O_2 complex using the Hamiltonian of a $^3\Sigma$ state for Hund's case (a), since the observed transitions are assigned to the series of the $K_a = 0$ component.

The Hamiltonian can be expressed as

$$\mathbf{H} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{sr}} + \mathbf{H}_{\text{ss}} \quad (1)$$

Table 1. Observed transition frequencies (in MHz) of H_2O-O_2 (upper part) and D_2O-O_2 (lower rows) and difference with the frequencies calculated using the Hamiltonian in the $^3\Sigma$ state for Hund's case (a) and K = 0. N, J and F represent the rotational angular momentum, the total angular momentum and the total angular momentum including nuclear spin, respectively.

Transition N'	J'	F'	N''	J''	F''	Obs. Freq. (MHz)	Obs.-Calc. (MHz)
H_2O-O_2							
2	2.0	1.0	1	1.0	1.0	14520.0732	−.0697
2	2.0	2.0	1	1.0	1.0	14520.8316	−.0573
2	2.0	3.0	1	1.0	2.0	14519.6794	−.0905
2	2.0	1.0	1	1.0	.0	14521.2234	−.0385
2	2.0	2.0	1	1.0	2.0	14518.5576	−.0934
2	2.0	2.0	1	2.0	1.0	17839.8957	.0222
2	2.0	3.0	1	2.0	2.0	17839.5000	.0785
2	2.0	4.0	1	2.0	3.0	17838.9337	−.0676
3	3.0	2.0	2	2.0	2.0	21755.9556	.0793
3	3.0	3.0	2	2.0	3.0	21755.3957	.0789
3	3.0	4.0	2	2.0	3.0	21756.1194	.0567
3	3.0	2.0	2	2.0	1.0	21756.7120	.0898
3	3.0	3.0	2	2.0	2.0	21756.5144	.0787
3	4.0	3.0	2	3.0	2.0	24090.4179	−.0783
3	4.0	4.0	2	3.0	3.0	24090.1436	.0237
3	4.0	5.0	2	3.0	4.0	24089.8048	.0263
4	4.0	3.0	3	3.0	2.0	28963.7677	−.0162
4	4.0	4.0	3	3.0	3.0	28963.6508	−.0212
4	4.0	5.0	3	3.0	4.0	28963.4508	−.0347
4	4.0	3.0	3	3.0	3.0	28963.2342	.0353
4	4.0	4.0	3	3.0	4.0	28962.9613	.0098
D_2O-O_2							
2	2.0	1.0	1	1.0	1.0	13419.5779	−.0289
2	2.0	2.0	1	1.0	1.0	13419.6962	−.0331
2	2.0	2.0	1	1.0	2.0	13419.3506	−.0245
2	2.0	3.0	1	1.0	2.0	13419.5144	−.0326
3	3.0	3.0	2	2.0	2.0	20111.9415	.0765
3	3.0	3.0	2	2.0	3.0	20111.7272	.0341
3	3.0	4.0	2	2.0	3.0	20111.8461	.0415
4	4.0	3.0	3	3.0	2.0	28963.7677	.0106
4	4.0	4.0	3	3.0	3.0	28963.6508	−.0204
4	4.0	5.0	3	3.0	4.0	28963.4508	−.0299

$$= B\mathbf{N}^2 - D\mathbf{N}^4 + \gamma \mathbf{N}\cdot\mathbf{S} + (2/3)\lambda(3S_z^2 - \mathbf{S}^2) \tag{2}$$

where $\mathbf{N}$ is the angular momentum of the rotation and $\mathbf{S}$ is the electron spin. γ and λ are the spin-rotation and spin-spin coupling constants, respectively.

The following hyperfine terms were included in addition to Eq. 2 due to the two hydrogens of water vapour:

$$\mathbf{H}_{\text{hfs}} = b_F \mathbf{I}\cdot\mathbf{S} + c/3(I_z S_z - \mathbf{I}\cdot\mathbf{S}) \tag{3}$$

where b_F and c represent the Fermi contact interaction and the dipole-dipole interaction constants, respectively. The calculated transition frequencies were fitted to the experimental values through a least squares fitting procedure. The molecular constants thus determined are listed in Table 2 for both the H_2O-O_2 and the D_2O-O_2 complexes. B_0 and D_0 are the rotational constant and the centrifugal distortion constant in the vibrational ground state ($v = 0$), respectively. λ_0 is the spin-spin coupling constant (also for $v = 0$), while λ_D is the centrifugal distortion constant for the spin-spin coupling.

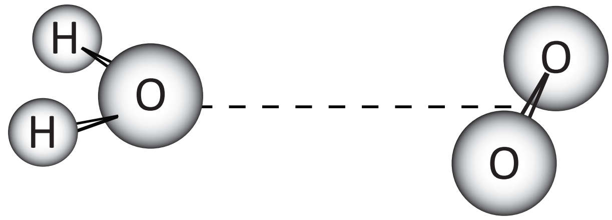

Fig. 2. Molecular structure of the van der Waals complex H_2O-O_2 determined to be C_{2v} by PN-FT microwave spectroscopy.

Table 2. Molecular constants in MHz for H_2O-O_2 and D_2O-O_2. For the D_2O-O_2 calculations, λ_0, λ_D and γ were fixed to the H_2O-O_2 values (left column).

		H_2O-O_2	D_2O-O_2
B_0	=	3633.197(14)	3357.211(13)
D_0	=	0.39942(84)	0.29293(49)
λ_0	=	64136.0(19)	—
λ_D	=	0.051673(fixed)	—
γ	=	−1997.924(49)	—
b_F	=	−1.82(23)	−0.28
c	=	6.09(36)	0.94(15)

2.3 Molecular structure of the H_2O-O_2 complex

The values of the rotational constant B_0 for H_2O-O_2 and D_2O-O_2 were found to be 3633.197(14) MHz and 3357.211(13) MHz, respectively. The difference between these constants indicates a C_{2v} structure with the two hydrogens of the water molecule in an outer position, as shown in Fig. 2. The direction of the complex axis is perpendicular to that of the molecular oxygen axis, as indicated by the symmetry of the complex, where the electronic ground state is anti-symmetric with respect to the C_2 rotation about the complex axis. These values of B_0 with the C_{2v} structure are consistent with the theoretical ab initio calculations of Sabu et al. (2004, 2005), but not with the C_s structure of Svishchev and Boyd (1998). Details of the comparison of the rotational constants obtained in our experiment with these obtained by ab initio calculations are described in Sabu et al. (2004). Therefore, we concluded that the molecular structure of H_2O-O_2 is C_{2v} in the vibronic ground state.

3 Estimation of K_p

3.1 Determination method and previous studies

Aside from atmospheric observations, there are two main approaches to estimate the equilibrium constant: direct measurement in the laboratory or estimation with statistical thermodynamics.

In the statistical thermodynamics approach, K_p is calculated using Gibb's free energy ΔG from the equation $K_p \cdot P = \exp(-\Delta G/RT)$, where R is the universal gas constant and T the temperature. ΔG is calculated as $\Delta G = \Delta H - T\Delta S$. Here, ΔH and ΔS represent the change in enthalpy and in entropy, respectively, for the formation of the complex at a total pressure P and temperature T.

In the case of H_2O-O_2, K_p depends on the temperature and on the binding energy between H_2O and O_2 through ΔH, while ΔS uses the partition functions obtained from the rotational, vibrational, and electronic energy level structures of H_2O-O_2, H_2O, and O_2. A more detailed description is given elsewhere (Vaida and Headrick, 2000; Kjaergaard et al., 2002; Sabu et al., 2005).

3.2 K_p obtained with the anharmonic approach

The studies of Vaida and Headrick (2000) and Kjaergaard et al. (2002) both used the harmonic oscillator approximation to calculate the partition functions needed to estimate K_p. Alternately, Sabu et al. (2005) calculated the partition function, and thus K_p, using another approach. They carefully examined all inter- and intra-molecular vibrations and evaluated the anharmonic levels below the dissociation limit (Sabu et al., 2005).

These estimated K_p values are plotted against temperature in Fig. 3. From this figure, it is easy to notice the limitations of the harmonic oscillator approximation in estimating the equilibrium constant. The K_p of Vaida and Headrick (2000) shows a peculiar increase, almost linearly proportional to temperature. The K_p values of Kjaergaard et al. (2002) have a minimum around 225 K and increase at high temperatures, indicating no dissociation of the complex. In both cases the behaviour of K_p is not compatible with the estimated structure of the H_2O-O_2 complex.

In sharp contrast, only the anharmonic estimate of K_p monotonically (exponentially) deacreases with increasing temperature. The absolute values of K_p are much smaller than the other estimates, because of the low binding energy and the small number of bound states. On the basis of K_p decreasing correctly with temperature, the inferred volume mixing ratios of the H_2O-O_2 complex at atmospheric temperatures are 1–2 orders of magnitude lower than those calculated by the harmonic approximation (Sabu et al., 2005).

It is worth emphasizing that only the calculations of K_p from Sabu et al. (2005) show a correct decrease with increasing temperature. Therefore, this set of values is the best estimate of K_p for H_2O-O_2 among the data currently available.

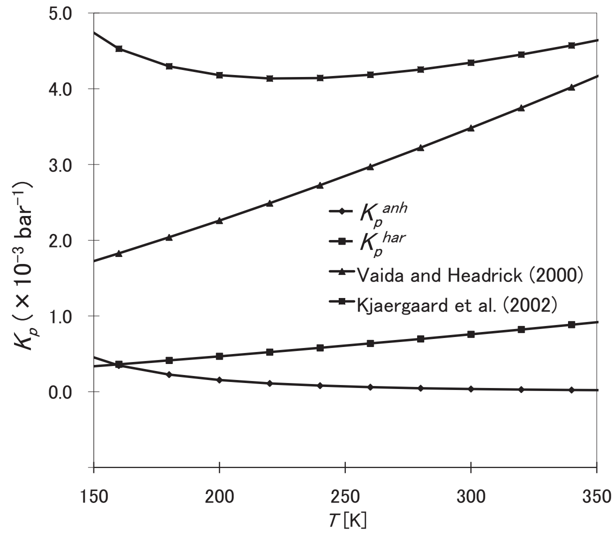

Fig. 3. Calculated equilibrium constant K_p for H_2O-O_2 using different methods (after Sabu et al., 2005) . The uppermost line (small square symbols) shows the results of Kjaergaard et al. (2002) and the triangle symbols those of Vaida and Headrick (2000). The lines with lozenge and big square symbols are the results of the anharmonic and harmonic calculations of Sabu et al. (2005), respectively.

4 Atmospheric abundance of the H_2O-O_2 complex

The atmospheric abundance of the H_2O-O_2 complex is represented by the equilibrium equation given below:

$$[H_2O]+[O_2]+[M] \rightleftharpoons [H_2O\text{–}O_2]+[M]. \tag{4}$$

From Eq. (4) we can infer the atmospheric partial pressure of the complex:

$$\left(\frac{P_{H_2O-O_2}}{P}\right) = K_p \cdot P \cdot \left(\frac{P_{H_2O}}{P}\right)\left(\frac{P_{O_2}}{P}\right), \tag{5}$$

where $(P_{H_2O-O_2}/P)$, (P_{H_2O}/P), and (P_{O_2}/P) are the partial pressures of the H_2O-O_2 complex, H_2O and O_2, respectively, for a given atmospheric pressure P. The partial pressure for a given molecule is related to its volume mixing ratio (VMR) by $\mathrm{PP} = \mathrm{VMR} \times P_{\text{dry air}}$. K_p is the equilibrium constant. The abundance of H_2O-O_2 is proportional to K_p and to the abundances of water vapour and of molecular oxygen (and inversely proportional to P).

4.1 Calculation setup

The H_2O-O_2 VMR distribution was derived from the partial pressure calculated using Eq. (5). We used the K_p values calculated by Sabu et al. (2005) with the anharmonic oscillator

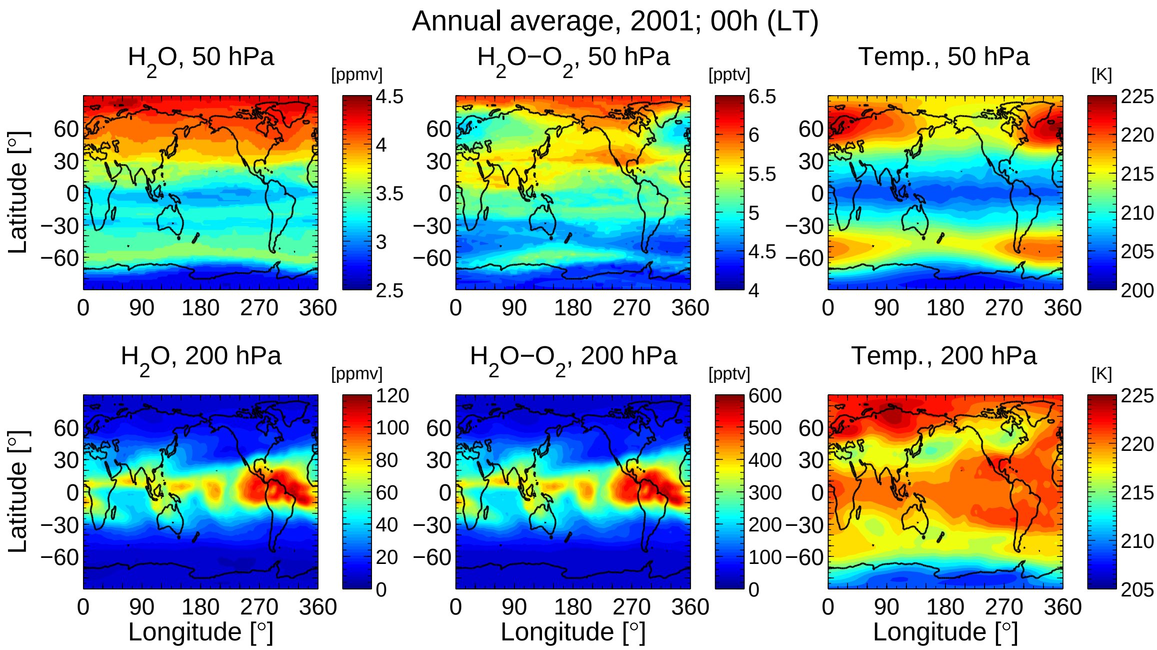

Fig. 4. Global distribution in latitude/longitude of the H_2O (left) and H_2O-O_2 (middle) VMRs and of the atmospheric temperature (right). The annual averages for 2001 at 0 h (Local Time) are shown at 50 (top) and 200 (bottom) hPa (∼21 and 12 km, respectively). The temperature data and the specific humidity field used to derive the H_2O VMR are taken from the ERA-40 reanalysis of the ECMWF data (see text). The VMR of the H_2O-O_2 complex is calculated using the equilibrium equation (Eq. 5), with the K_p values derived from Sabu et al. (2005). The horizontal grid sampling is $2.5° \times 2.5°$.

approximation, tabulated as a function of temperature from 150 K to 350 K with a step of 5 K.

The partial pressure of O_2 was set to a constant value at all levels, equal to 20.946 % of the dry air pressure. The temperature, pressure and specific humidity were taken from the European Center for Medium-range Weather Forecast (ECMWF) ERA-40 reanalysis dataset (Uppala et al., 2005). The ERA-40 data fields, sampled on 23 pressure levels from 1000 to 1 hPa, are provided as monthly averages at 0 h, 6 h, 12 h and 18 h (Local Time) on a latitude/longitude grid with a $2.5° \times 2.5°$ horizontal resolution.

For this study we calculated an annual average for 2001 at 00:00 h LT, sufficient to assess the usefulness of the K_p measurements for atmospheric applications. Figure 4 shows the inferred global distribution of H_2O-O_2 (middle column) for the 2001 average, at 200 and 50 hPa (about 12 and 21 km, respectively). These height levels were chosen to illustrate the difference between the tropospheric (200 hPa) and stratospheric (50 hPa) distributions of the molecular complex. For comparison the distribution of the water vapour VMR and of the atmospheric temperature are given at the same heights.

4.2 Distribution of H_2O-O_2

From Fig. 4 it is possible to get some qualitative understanding of the distribution of the H_2O-O_2 complex. Two different behaviours can be identified. In the upper troposphere (represented by the 200 hPa level, lower row) the VMR of the complex is strongly correlated to the water vapour amount. The H_2O-O_2 VMR is largest in the equatorial region and small in the mid- and high latitudes of both hemispheres. This corresponds very well to the water vapour distribution, whereas the temperature is highest at Northern high latitudes.

Above the tropopause (50 hPa level, upper row), the situation is different. Temperature has a marked minimum at the Equator, where there is also little H_2O or H_2O-O_2. Conversely, at higher latitudes (from 30–40° in both hemispheres), there is an obvious correlation between high temperatures and low levels of H_2O-O_2: the VMR of the molecular complex seems inversely proportional to the atmospheric temperature, while the water vapour distribution is rather homogeneous with large values in the Northern Hemisphere and small values in the Southern Hemisphere.

The inferred abundance of H_2O-O_2 in the Earth's boundary layer (1000 hPa, not shown) ranges from 1 to about 250 ppbv. This is comparable to CO (∼200 ppbv) or to N_2O (∼300 ppbv). Estimating the abundance of water vapour complexes is therefore important for tropospheric chemistry.

5 Summary

We performed laboratory spectroscopic experiments for the H_2O-O_2 complex and determined its molecular structure. The result differs from the potential minimum-structures but agrees well with that calculated by the anharmonic oscillator approach, which increases our confidence in the quality of the K_p estimated by the same method. Using these high-quality values of K_p allowed us to provide a first (theoretical) estimate of the atmospheric distribution of H_2O-O_2. The inferred abundance of H_2O-O_2 at the Earth's surface is at the sub-ppmv level. This is comparable to the surface concentrations of CO or N_2O and shows that knowledge of the abundance of water vapour complexes is undeniably important to further our understanding of tropospheric processes.

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