Interactive comment on “The H$_2$O–O$_2$ water vapour complex in the Earth’s atmosphere” by Y. Kasai et al.

Y. Kasai et al.
ykasai@nict.go.jp

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Reviewer’s comment:
>>The FTMW of the H$_2$O-O$_2$ complex has been recorded to determine its structure. Previously determined Kp values for the complex were used to assess its abundance in the Earth’s atmosphere. It is my impression that there is not sufficient new material in this paper.

Answer to the comment:
The new scientific results we reported in this paper are:
1. The first observation of the H$_2$O-O$_2$ microwave spectroscopy.
2. The first determination of the “averaged” structure of H$_2$O-O$_2$ with isotope observation by experimentally. Determination of the structure is important to estimate precise Kp of the reaction [H$_2$O-O$_2$] + [M] ⇔ [H$_2$O] + [O$_2$] + [M] by thermal statistical method.
3. The first global distribution of water vapor complex by using Kp estimated with “the most precise estimation under the present research”. We found the wide range of the abundance in the distribution at same pressure height, for example, 100ppt (polar region) - 600ppt (equator region) in 200hPa. We also shown that H$_2$O complex is abundant as same level of CO and NO2. That means that the abundance of H$_2$O complex is among ten most abundant species in the boundary layer.
4. People believed the global distribution of water complex is only depends on the water vapor distribution. We shown the different case in tropopause region. The global distribution of water complex is depend on the temperature, not the water vapor distribution in tropopause region because of its temperature minimum.
We have four new scientific results on the paper.

Reviewer’s comment:
>>The FTMW structure is determine to be C$_2$v. Previous ab initio calculation (Robinson 2003, Sabo 2004 2005) agree that the minimum on the ab initio surfaces is Cs with the O$_2$ attached to an H atom. The observation of the C$_2$v structure in the MW is explained as the average and is a reasonable explanation. However, this has already been mentioned in the conclusion of Sabo 2005 “The feasible feature of the disrotatory vibration is responsible for the C$_2$v symmetry of the complex inferred from the FTMW spectrum”. Thus, I’m not sure what is new here?

Answer to the comment:
Sabu (2005) described about our experimental result that the structure of H$_2$O-o2 is C$_2$v with only one line in his full paper. I think one line is not enough to show the
scientific result. This paper is the first report to the journal about the structure of H2O-O2 complex by the isotope experiment. We do not ignore the part of the description about Kp in the paper, because we wanted to explain the reason why the spectroscopic measurement is important to estimate the global distribution of H2O-O2. Detail scientific report was described in Sabu 2005. In the paper, we described it only briefly. We used only less than 1 page (page 10075) of total 18 pages (page 10069-10086). This part is definitely NOT the scientific report result of this paper. That should be clear in the paper since we referred the references (Sabu 2005), and used only less than one page.

Reviewer's comment:
>Also, both harmonic and anharmonic methods are probably not very accurate, and as far as I know no experimental values for Kp of this complex has been measured yet – thus there is still significant uncertainty in Kp.

Answer to the comment:
Harmonic method do not take into account the anharmonic potential curve between an inter-molecular vibration, that give no dissociation of the inter-molecular vibration. In harmonic method, H2O-O2 complex never dissociate with vibration between the H2O and the O2, and that is not realistic in the atmospheric temperature. The anharmonic method take into account this dissociation. The anharmonicity of the potential curve is fundamentally important to know the physics of the molecule. For example, if you do not take into account the anharmonicity of the potential curve of the molecules, you can’t calculate the cross section of the transition of the molecular spectrum. Anharmonic method is more realistic. Details are described in Sabu 2004 and Sabu 2005. There are no reason why both harmonic and anharmonic methods are probably not very accurate after two papers were accepted in this topics. Anharmonic method is reasonably more accurate than the harmonic method. On the other hand, there are no method to validate the accuracy of the Kp. Accuracy and precision of the Kp determined by laboratory experiment is also not very high. That is why it is important to detect H2O complex in the atmosphere to determine “the atmospheric amount of water vapor complex”.

Reviewer's comment:
>The result that atmospheric VMR depends strongly on water concentration (which depends strongly on temperature) is as I would expect. Minor comments: p. 10077, line 13, I don’t understand the second half of this sentence “This corresponds very well to the water vapour distribution, whereas the temperature is highest at Northern high latitudes”

Answer to the comment:
As we shown in Figure 4, and mentioned in the first answer for the reviewers comments, we shown both 1) Distribution of H2O-O2 complex is depend on that of the water vapor in the troposphere, and 2) Distribution of H2O-O2 complex is inversely correlated to that of the temperature in the tropopuse. This paper give an important information where we have to search to detect the atmospheric water vapor complex.

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