

## ***Interactive comment on “Detection of organic compound signatures in infra-red, limb emission spectra observed by the MIPAS-B2 instrument” by J. J. Remedios et al.***

**J. J. Remedios et al.**

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Referee 1

We thank referee 1 for very positive comments and an appreciation of the essential points of the paper.

1. Pg. 10024, line 24: Is the detector an arsenic-doped silicon detector (blocked impurity band), i.e., Si:As BIB? If so, then the text needs to be corrected.

The text will be updated to read "and a four channel liquid-helium-cooled detector de-war. The detectors are arsenic doped, silicon blocked impurity band detectors (Si:As BIB)."

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2. Pg. 10028, line 4: the Greek nu is missing a tilde.

Thank you.

3. Pg. 10030: The aerosol part of the retrieval is clearly important because it interferes with the bands of interest. Could a little more information on it be supplied? For example, is aerosol extinction assumed to be without structure or is it assumed to be sulphate with appropriate spectral structure?

The aerosol information has been retrieved from as close as possible to the target regions and assumed to have flat spectral structure in the vicinity of the organic compound signatures. For example, for formic acid, the residual baseline provides a very good indication of the likely quality of the inferred spectral signatures as can be seen from the figures.

The text has been modified to read (section 3.1, p.10029, line 4) "The spectral baseline close to each target spectral feature was a particular indicator of the quality of the fit and minimised principally using aerosol extinction (assumed spectrally flat in the vicinity of the target spectral signatures); there is also a contribution from heavy molecules such as CFC-12 and HCFC-22 for which the band shape can be fitted (Sect. 4.4)."

4. I find the agreement between observed and calculated residual spectra to be satisfactory and convincing. One aspect, however, puzzles me somewhat. I expected that the calculated residual spectra would be smoother. In fact, the calculated residual spectra often show sharp structure, which I am assuming is due to the radiative transfer part of the simulation. Perhaps a comment on this point would be helpful.

This point was already made in Section 3.1 Paragraph 2: However we have tried to expand the statement at line 16 (p.10028) to clarify further. The line now reads: "Even for  $\Delta F$ , the appearance of residual spectral features of interfering gases is intrinsic since the presence of strong interfering gas lines alters the contribution of the target gas where the combination of these effects is non-linear, e.g. near the centre of

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saturating lines. In such cases, there will be incomplete cancellation on wavenumber scales of the order of the widths of interfering gas lines in  $\Delta F$  and hence residual structure."

5. Acetone lab data used in the retrievals should be published. Is there a paper in preparation? If so, it might be good to say so. If not, then this is a problem because other workers cannot retrieve acetone from their spectra to verify and extend the work reported here.

Yes, there is a paper in preparation and we have amended the text to note this. We also note that the Waterfall reference does apply to a publically available thesis. p. 10029, line 27 now reads "from Waterfall (2003) for acetone; the acetone measurements are in preparation for a paper to be submitted shortly."

Referee 2

The referee notes that the paper is appropriate for ACP which is a statement with which we would agree.

1. I would like to see the retrieved profiles as Figures from the lowest detection altitudes upwards, may be up to the tropopause.

We understand why the referee might think of such a figure and have therefore included one here within a new section 4.5 which summarises the detection result (although in fact all the information is in the text). The new Figure is Figure 10 and we have included this within a new section 4.5:

Caption for Figure 10: Figure 10: Inferred concentrations for PAN, acetone and formic acid as a function of altitude (MIPAS-B2 flight 6). Error bars are estimated random errors, as described in section 5, arising from the noise equivalent spectral radiance at each altitude and in each channel (channel 1 only for the PAN profile plot).

We have also corrected the statement at line 9 on p.10029 to read: "results are presented here only for altitudes where inferred concentrations were not so constrained

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by noise as to arise only from the initial a priori information."

We should note that we do not believe that the new figure for the "profiles" contains any more geophysical information than is already available by stating the values in the text but it is good for visualisation. Also, comparison with literature values has already been presented in the paper and the literature is relatively poor compared to the variability of these compounds. Of course, in future the values in this paper will help to provide a basis for future literature comparisons for the Mediterranean region which is one of considerable interest.

2. We have updated "free troposphere" to the "mid-latitude upper troposphere" in the abstract.

3. The title should contain the word balloon, to distinguish it clearly from the MIPAS satellite instrument, the abbreviation -B2 is not sufficient.

Yes, the new title is "Detection of organic compound signatures in infra-red, limb emission spectra observed by the MIPAS-B2 balloon instrument"

4. Why did the authors use the HITRAN 2000 database, and not HITRAN 2004?

The majority of this work was performed prior to release of HITRAN 2004 but the updates in that database have no substantial impact on this work.

5. I do not see the advantage of using the Norton-Beer strong apodisation, except of creating smooth spectra. The apodisation chosen decreases the resolution to half of its original value. A short clarification would be useful.

For weak broad-band cross-section signatures such as those for PAN and acetone, high spectral resolution is not critical but distortions of the wavenumber dependent signature due to sidelobes of multiple interfering strong lines are important. Therefore apodisation is important and appropriate given a relatively modest reduction in spectral resolution. We have amended the text on p.10025, line 22 to read: "interpolated to a sampling grid of 0.025 cm<sup>-1</sup> using zero-filling of the measured interferogram. The

apodisation is particularly useful for detection of weak cross-sectional species, such as acetone and PAN, where it is not so critical to achieve the highest spectral resolution but rather it is necessary to reduce the impact of sidelobes of multiple strong interfering spectral lines on the regions between spectral lines. This allows for a cleaner detection of the wavenumber dependence of the target spectral signatures".

Comment by Thomas Von Clarmann

We thank Dr. Von Clarmann for his helpful technical remarks.

1. Matching of residual spectra rather than minimization of residuals.

We clearly need to further improve our description of the process in Section 3.1. For confirmation that the spectral signature has been detected, rather than retrieved, we prefer to identify the expected signature from the spectra rather than show simply that the residuals are improved. Although these processes are mathematically equivalent, our  $\Delta F$  and  $\Delta Y$  demonstrate visually the signature of the target species as opposed to  $R_F - R_y$  which does not. We are comparing  $\Delta F$  (ideally equal to simulating target gas signature) with  $\Delta Y$  (ideally equal to the observed target gas signature) to show that we see matching signatures in both. The ideal  $R_F - R_y$  is zero but in reality would be a noisy residual which does not demonstrate the gas signature directly. We are sure that our approach is well suited to our purpose.

Dr. Von Clarmann is mistaken in that we do not claim the method is superior to minimization of residuals just more suited to our purpose which is to demonstrate detection. He is correct, however, that the method employs interactive, iterative fitting with visual inspection of  $\Delta F$  and  $\Delta Y$  to demonstrate detection as opposed to completely automated algorithmic fitting, more suited to global retrievals.

To be more clear, we have therefore amended Section 3.1 as follows: Bottom of p.10027, top of p.10028: "Therefore, in order to demonstrate spectroscopic detection via a visible spectral signature for the target gas, we seek to compare/match quantities

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(defined here as “residual spectra”) displaying the target features in both measured and simulated equivalents rather than simply minimize (ideally zero plus noise) the residual of the measurement and its simulation."

We have also modified the bottom of p.10028 to read: "The primary means of performing this process was iteration of the expected gas concentrations and aerosol extinctions from an initial, a priori state, using Jacobian perturbation spectra scaled to match the residuals in a manner analogous to a formal inversion process but employing visual inspection of the residuals and interactive adjustment of the scaling."

## 2. Error simulations

Dr. von Clarmann is quite right in that the link between the estimated error calculation and the errors for detection was a little confused in our original section 5 which was trying to estimate these but also consider theoretical limitations on errors. We have updated section 5 to include a more comprehensive error analysis with two cases of theoretical simulated error involving joint retrievals and a specific estimate of error for the detection process based on the residuals of the spectra. Section 5 has therefore been improved considerably beyond its original objectives but should be even more useful to readers.

### a. Constraints on the retrieval

We have already noted the effective constraint in section 3.1 at line 10028 as described above in reply to point 1. We had further noted in section 5 p.10037, line 5, the following statement: "Since the detection method incorporates an effective a priori profile through the initial guess, which in this method constrains both expected values and profile shapes, the gain matrix for detection is estimated formally using the optimal estimation approach (Rodgers, 2000)"

We believe that our method uses an effective a priori constraint and hence the optimal estimation method provides a good approximation for the errors. We have modified

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section 3.1 to be also more explicit on this point and to be consistent with Section 5. For Section 3.1, p.10028, the section now includes the statement. "; the initial atmospheric profile also acts as a constraint here for both values and profile shape in a similar manner to definition of a formal a priori in optimal estimation".

b. Gain matrix referring to entire retrieval rather than individual profile levels.

Thank you. This is a just a lack of clarity in notation and statement in Section 5. We now refer explicitly to the fact that the matrices are only evaluated at one height,  $z$ , so that no vertical correlations are present in the calculations. Also the variable,  $z$ , is included in all the Equations.

c. Additional variables should be treated as aspects of the joint retrievals.

This is a good point and our case (2) now considers the case explicitly where all the major parameters are retrieved simultaneously from a broad spectral region. For the detection process, we reflect on the fact that the fits of the other species are not perfect and some residual structure remains in the radiances.

Yours sincerely,

John Remedios

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10021, 2006.

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