Interactive comment on “First atmospheric observations of three chlorofluorocarbons” by J. C. Laube and A. Engel

Anonymous Referee #2

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General comments: This paper represents the potential detection of three unsaturated alkenes in the remote atmosphere. It is believed that short-lived chlorinated and brominated gases can indeed contribute to the ozone-depleting halogen burden of the stratosphere and so quantitation of such influences is warranted. Much should be improved in this manuscript, however, before publication is warranted. Improvements related to better proving that these compounds were indeed responsible for the signals detected are needed, as is a more balanced approach to discussing implications of the results, if indeed they are borne out by some careful additional analytical chemistry.

Specific comments: Though the authors have done a commendable job minimizing sampling influences by forgoing pumps and other procedures, they need to do additional work to better identify the unknowns detected. Standard procedures for identify-
ing unknown analytes generally involve checking retention times of the unknown with a synthetic sample, sometimes even on multiple columns with very different separation characteristics. Mass spectrometry is a very useful tool, yet the assertion that all ions were observed "in expected abundances" (p. 6686) is not borne out as true from a comparison of the spectra and indicated ‘expected abundances’ made available in the figure caption. Given this assessment of the comparison here, it is not clear what is meant by the text that the other spectra "agreed perfectly" with expectations (line 25 of same page). Without this additional cross-checking, the main conclusion of the paper is suspect.

Standardization of the compounds here is very crude, yet serves a useful purpose. Identifying a range of possible sensitivities based on other compounds provides a step forward. The implication in my mind, however, is nearly opposite to what the authors suggest. It seems likely that the results presented indicate that these compounds will deliver a negligible amount of chlorine to the stratosphere. The data these authors have collected suggest that mixing ratios are likely to be extremely small in the remote atmosphere and in the free troposphere, yet they argue that these compounds should be monitored because they may contribute significant amounts of halogen to the stratosphere. This does not seem likely, and it does not seem to be a necessary argument. It is a fine and useful conclusion to draw from an initial study that the ozone-depleting halogen contribution of these new gases is likely to be small; there is no need to overestimate their importance (as is done now, in my mind).

Finally, some of the manuscript is overly brief, imprecise, or unclear. Were detectors placed in parallel? Would one expect COF2 and these other products to be analyzable in the instrument used? Don’t potential co-elution influences suggested for CFC-12 hinge critically on the ion used? Aren’t mixing ratios in most samples quite small, and wouldn’t you expect them to be even smaller in the tropics? And therefore isn’t it likely that any contribution of these gases to Cl in the stratosphere should be small? Surely other compounds that are good indicators of anthropogenic input were measured from
these samples, what do they say about the processes influencing these air samples? Are the smallest responses observed in the cleanest air?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6683, 2008.