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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “SO_2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols” *by* A. R. Whitehill et al.

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Review of: SO2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols by Whitehill, Jiang, Guo and Ono

This paper describes a series of experiments into the S-MIF pattern produced by SO2 photochemistry, with emphasis on photolysis. It is asserted that SO2 photolysis is responsible for the S-MIF signal observed in some volcanic sulfate in polar ice cores because some of the SO photoproduct combines with O2 in the atmosphere in a three body reaction to form SO3 which reacts with H2O to produce H2SO4. The rate of this reaction is poorly constrained (the only evidence is one determination in the literature of an upper limit) and an effort is made to estimate it's rate. Stationary points on the SO3 potential energy surface are investigated using quantum chemistry, and a chemical box model is used to interpret the experimental results. The paper describes a well-designed set of experiments and painstaking isotopic analysis. There is a lot of interesting material here that makes it a pleasure to read and a valuable addition to the field. I have a few concerns detailed below that should be addressed prior to publication.

Scientific comments

The Introduction is very well written and gives a readable review of current understanding in the field. In 23501, 23 (page, line) it is stated that the experimentally measured 1% KIE for 34SO2 reaction with OH relative to 32SO2 is incompatible with Castleman's measurement of 1974. First, note that this is a single measurement 40 years ago, good work but it includes some uncertainty. More importantly, the experimental measurement was done in the range of -20 to +40 C and does not include the temperature at which the SO2 + OH oxidation took place high in the atmosphere. One must extrapolate the measured KIEs outside the range of the study without a reason to think the temperature dependence of the KIE would be linear. Overall, given these issues, it is speculative to say the experiment and the field measurement do not agree. Suggest more cautious language - perhaps there is an indication, but nothing as clear cut as the text appears to claim.

There must be some water in the photoreactor, in order to convert SO3 into H2SO4. There is always some water on anything that has been open to the atmosphere, including anything that has not been pumped out under high vacuum for many days. How much water? Was OH produced via water photolysis or O(1D) plus H2O?

23500, 27, why 'requires a high SO2 column density'? Not clearly argued in the text. Please discuss how 'requires' is meant - does this mean a large amount of

SO2 between the place where SO2 is photolysed and the sun, in order to ensure self-shielding? Or, simply that there is enough SO2 present in a plume to ensure a signal?

23500, 27, why 'an SO2 plume reaching an altitude of 25 km or higher'? This limit seems somewhat arbitrary. According to Figure 8, 20 km should be sufficient. Including uncertainties, could it not simply say, 'above the tropopause'?

For example at 23514, 12. Isotope selective intersystem crossing due to an accidental near degeneracy is a plausible theory with some evidence to back it up. It is an advance to the field. However, it will act at the same time as other mechanisms including self-shielding and the rate of photoabsorption (isotopologue-dependent cross section), not instead of them. The overall effect will be a combination of the basic mechanisms.

Section 4.2. The 'Ran-Lyon' model uses isotope-dependent vibrational frequencies to derive shifts, and the isotopologue-dependent absorption cross sections are obtained as shifted versions of the 32SO2 absorption cross section. This approach does not take into account changes in the Franck-Condon factors observed by Danielache et al., or changes in the rotational constants/rotational fine structure. This is important when calculating self-shielding. The agreement with experiment is fine, but keep in mind there is more to the story and the model may have gotten the right answer for the wrong reasons.

The model and the discussion do not consider HOx chemistry, and they do not consider photochemistry of the reduced sulfur compounds. Polysulfur product is extracted and analyzed, and so some additional reactions must take place: S + S2 + M –> S3 + M; oxidation of reduced sulfur, photolysis of polysulfur species, etc. Any of them could reasonably give S-MIF in analogy to the oxygen reactions (for example ozone formation, ozone photolysis, etc.). In Figure 6, for the no oxygen case, why don't the sulfate and the elemental sulfur show mass balance of the isotopes, equal and opposite D33S? If SO2 photolysis is the source of both S_n (polysulfur) and sulfate, why don't they have the same D33S?

Is equation (7) for the spectral irradiance of the lamp independent of the distance from the lamp? What is the uncertainty in this empirical equation?

23522, 7, Tunneling of oxygen and/or sulfur should not have any effect at all on the rates of these reactions. Please omit this throw-away explanation.

23522, 27, on the fly transition state hopping calculations would ('in theory') be able to derive rate constants without the need for global PESs.

Section 4.6. First: Three body reactions get faster as temperature decreases. What is the temperature dependence of R6? Second: The discussion in this section ignores the potential role of photoexcitation – the light flux in the photoexcitation range is much larger than in the photodissociation range. Please include and discuss.

23525, 20, Since the Lyons results are do not give accurate high resolution rovibronic structure, how can they give an accurate prediction of self-shielding? The rotational fine structure is very important for self-shielding.

23526, section 4.7, given the actinic flux spectrum and the SO2 absorption spectrum, it is beyond doubt that photoexcitation will take place. This process very likely has an isotopic signature. What is there to say that photoexcitation and photodissociation do not occur simultaneously?

In Table 2, why is there such a large difference between the values obtained in the first and second experiment at each temperature? In each case there is a significant drop in d33S, d34S, d36S. Please discuss. Could S chemistry play a role?

Table 3, do the organosulfur product enrichments match the predictions of Danielache et al.?

Table 4, it is suspicious that there is a negative trend in k(R6) as the oxygen pressure increases. The model includes O2 pressure and Ox chemistry, so in theory, this trend should not be here. Why is the result so dependent on pO2?

Table 5, why are the two runs with each filter (200BP, 250LP) so different in terms of delta values? Please explain.

Table 6. The quantum chemistry results are used to make qualitative arguments and the level of calculations does seem adequate to this task. However, as seen here and in tables 7 and 8, the energies obtained using the different methods are very different. How should we know which one to believe, and is there any way to know that the ultimate method used in this paper is adequate to the task? What are the error bars on the resulting values?

Table 9, I do not see sulfate formation. How much water is there? What are the concentrations of the HOx radicals?

Figure 1. Very nice straight line. Does this need to be included, and as Figure 1? Perhaps it could be put in a supplementary infromation file, or better yet, left out. The equation and a short description are all that is needed.

Figure 3, very nice result.

Figure 7, left. The model always predicts increased f_R6 as O2 is increased, yet this is not observed in the experiments. Do you have an explanation? Why should we have believe the model and the resulting rate? The rate is not determined directly, but indirectly, via the model. This introduces many uncertainties (J value, completeness of model), and this difference is yet another indication that the model is not right. (The first, as noted above, was that the value of k varies with the oxygen content).

Technical comments 23500, 9, add colon: 'the two absorption band systems of SO2: photolysis..and photoexcitation..' 23504, 11, better to write 'transmittance at wavelengths longer than 190 nm'. It is not clear if 'above' refers to energy, wavelength, wavenumber, frequency, etc. 23505, 24, I don't see the need for introducing the non-standard abbreviation 'DCM' for dichloromethane (by the way, the abbreviation is de-

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fined twice in the text). It is used so few times, only on pages 4 and 5, so that if you really must shorten it, why not write CH2Cl2? 23509, 19, it is too strict to write '=0'. There is a range of values that would be considered mass-dependent. Suggest either 'approximately equal' or to give the range. 23512, 22, this sentence does not use a parallel construction as the first have is an expectation and the second half a seeming statement of face. Should the second part rather be, 'but are not expected to reproduce'? 23514, 20, there's not a clear dividing line between chemistry and physics, so it's not clear what is meant here in making a distinction between photochemistry and photophysics. Please rewrite using different terminology. 23514, 25, it is not clear what is meant by 'overprinting'. See comment above under scientific comments, 23514, 12. 23529, 5, the rate given here does not agree with the range of values given in the abstract, please be consistent.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23499, 2014.

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