

Interactive comment on “Ultra-violet absorption cross sections of isotopically substituted nitrous oxide species: $^{14}\text{N}^{14}\text{NO}$, $^{15}\text{N}^{14}\text{NO}$, $^{14}\text{N}^{15}\text{NO}$ and $^{15}\text{N}^{15}\text{NO}$ ” by P. von Hessberg et al.

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Hessberg et al., UV absorption cross-sections of isotopically substituted N₂O

General comments

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This is an excellent, valuable and timely paper, providing the most fundamental data to date on the fractionation of N₂O isotopologues by UV photolysis. Isotopic fractionation in N₂O is a valuable tool for constraining the global N₂O source-sink budget. Kim and Craig (1993, see Hessberg et al for references) first noted that the back-flux of N₂O from the stratosphere to the troposphere must be isotopically heavy relative to tropospheric N₂O to balance the isotopically light N₂O sources at the earths surface.

In 1997, Yung and Miller suggested the mechanism: the heavier isotopologues are photolysed more slowly than the parent $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ by solar UV radiation, and thus become enriched in the stratosphere. Yung and Miller proposed a simple blue shift (due to the zero point energy) of the heavy-isotope absorption spectra, which then overlap less with the solar spectrum. This theory underestimated the observed fractionation by about a factor of two - subsequent theoretical studies (Johnson et al. 2001, Blake et al. 2003) improved the agreement but still left large uncertainties. Meanwhile a plethora of experimental studies (see paper) characterised the fractionation for single wavelength and broadband photolysis, and in the stratosphere, but still left relatively large errors and uncertainties.

The theoretical isotopic fractionation due to photolysis at any wavelength is best determined directly from the ratio of UV absorption coefficients of the heavy to light isotopologues. For stratospheric fractionation, the enrichment factors (wavelength and temperature dependent) must be multiplied by the solar actinic flux (wavelength and altitude dependent) and integrated. However until this paper, UV absorption cross sections in the most important spectral region have not been available. The paper thus provides the fundamental data on which measurements and models of N_2O fractionation in the laboratory and stratosphere can now be compared.

In this work, the UV cross-sections are determined from 181-218 nm at 233 and 283 K, representing stratospheric and surface temperatures. Measurements are made with two UV sources (synchrotron radiation and D2 lamp) and combined to provide the final spectra. The experimental methods are fully described and the enrichment factors calculated at 1 nm resolution. Errors are carefully controlled and quantified. The resulting enrichment constants are then compared with laboratory photolysis measurements, and used in a global 3-D model (previously published using enrichment factors based on theory) to compare with actual measurements of stratospheric fractionation. The quality and integrity of the work appears to be high. The paper satisfies all criteria for publication in ACP after minor corrections discussed below.

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Specific comments

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Experimental: Unfortunately, at both sites the spectrum was undersampled for the slitwidth (resolution) used sampling theory dictates that there should be at least 2 points per resolution element to fully represent the spectrum, or narrow features may be lost. The effective resolution is limited here to about 2 nm, but given the lack of structure in the spectra, this is probably not a serious limitation. The authors address this point adequately.

3.4.1 Comparisons with previous experiments (p2348, line 4)

As a co-author of Turatti et al., I have to defend the statement that the 207.6 and 211.5nm results from Turatti are in mutual disagreement. FTIR measurements are generally less precise than those from IRMS. The Turatti et al. enrichment factors stated in the paper are:

$\epsilon(456)$ $\epsilon(546)$

207.6nm -66.5 ± 5 -27.1 ± 6 per mil

211.5nm -65.3 ± 4 -31.4 ± 8 per mil

Within their stated error limits, these values are not in mutual disagreement or inconsistent with a negative value of $d\epsilon/d\lambda$. The sentence beginning with "However, it is noted..." should be removed. (This would also improve flow to the next paragraph.)

3.4.2 Comparisons with models The paragraph starting p2347 line 22 should be revised given that the paper by Morgan has now been published (2004 not 2003).

4. Modelling The updating of the McLinden et al 3-D model to use the UV cross-section-based enrichment factors instead of theoretical values is a strong point of this paper. In general the new experimental values of ϵ (photolysis) lead to more negative values of ϵ (apparent) than those previously published. In this sense they are also more in agreement with the values from the Morgan et al (2004) 2D model, and agree less

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well with the IRMS data.

Again, at the risk of seeming over-sensitive, I am bound to defend the FTIR occultation measurements of enrichment factors in the stratosphere. These are generally larger (more negative) than most IRMS-based measurements. Considering Figure 7, there is a clear bias of 4-5permil between L+C values and IRMS-based observations, with observations being less negative. FTIR occultation measurements (averaged over 11 profiles at a range of latitudes) show the opposite bias, around 7permil more negative than the L+C values. If the point of this section is to compare the model/L+C predictions with stratospheric measurements, as it is, I cannot see that it is justified to simply include the IRMS data (4-5permil lower) but reject the FTIR occultation data (7permil higher), as has been done. One might equally argue that including the FTIR data would improve the average agreement with the model! I recommend that the wording be changed to address this point.

The bias between IRMS and occultation measurements is a separate, quite valid issue which still needs clarification. We will address this difference in a forthcoming publication soon to be submitted.

Technical comments and corrections

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p2335 | 18 , but *laboratory* experiments.

p2335 | 15 Replace subsequently with consequently

p2336 | 6 Include reference to Morgan et al. (2004) model paper, now published. Note this paper publication year is 2004 not 2003.

p2337 | 14 Would be better to include ^{16}O explicitly in formulae

p2338 | 15 The gases used were:

p2339 | 4 in order to remove *non condensable* gases

p2340 | 2-3 An optical chopper was mounted before the beamsplitter and operated at 1000Hz. (Then leave out the sentence starting (The light and electrical signal...))

p2341 | 25 Specify the make and model of spectrometer/monochromator.

p2343 | 25 thus the water *vapour* content was essentially zero.

p2345 | 25 ...experimental data are those from...

p2349 | 26 This is quite a serious calibration disagreement 18 vs 46 permil for the 456-546 difference in air. Could there be a sentence giving the latest status? even if it is simply *This discrepancy is yet to be resolved*.

p2350 | 14/15 The use of LS and MS OK here, but the axis labels in Fig 6 use U (for upper?) instead of M. The legend says M.

p2351 | 24 Morgan (2004) check any other occurrences.

p2352 | 3 ...the model budgets, the (*mean, average, net? or appropriate*) enrichment constants for stratospheric loss can be calculated.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2333, 2004.

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