Detection of stratospheric nitrogen species

SIR—When Toon *et al.*¹ claimed a definitive detection of N_2O_5 in the stratosphere from atmospheric trace molecule spectroscopy (ATMOS) data, they showed only one absorption band that could be attributed to N_2O_5 . They claimed another band near $1,700\text{ cm}^{-1}$ was evident, but this claim might be thought dubious because there are strong overlapping bands of HNO_3 at $1,700\text{ cm}^{-1}$, which differ between Northern Hemisphere (sunset) and Southern Hemisphere (sunrise) spectra, and the authors did not show this other band. My own tentative measurement of N_2O_5 (ref. 2) has been described by Camy-Peyret and others as a measurement of “an N_2O_5 -like substance.” So far, the ATMOS detection could rightly be claimed to be one of “an even more N_2O_5 -like substance”, but it is not an unambiguous detection as the authors claim. The evidence for it being N_2O_5 is very good, but many constituents have P- and R-branch features like the observed absorption, and although none is known at the observed wavelength, chemists are not infallible at predicting which trace constituents will or will not exist.

Most spectroscopists would agree that a definitive identification can only be claimed when two isolated or well-resolved lines or bands are observed simultaneously. This point was clearly stated by Rinsland *et al.*³, who analysed balloon-borne spectra to search for absorption by $ClONO_2$ —they declined to claim a detection of $ClONO_2$ because they observed two bands, but on different balloon flights. This was left for the ATMOS team⁴ who analysed four bands of $ClONO_2$ and published two. The ATMOS team has clearly taken the point because its tentative detection of HO_2NO_2 (ref. 5), which consisted of one band only, was entitled “Evidence for the presence of . . .”.

Over a year has elapsed, and Toon *et al.* have still not published additional spectra to establish their claim. Yet they continue to assert that they have definitively measured N_2O_5 , most recently in a paper submitted to the *Journal of Geophysical Research*⁶. Furthermore, administrators

have accepted their assertions: in their 1986 report to the United Nations Environment Programme (UNEP), the Coordinating Committee on the Ozone Layer claimed that “the presence of the temporary reservoir species $ClONO_2$, N_2O_5 and HO_2NO_2 in the stratosphere has been definitively established by recent observations”. This is false on two counts.

I am as keen as anyone to establish that the broad absorption band observed in the atmosphere at $1,240\text{ cm}^{-1}$ arises from N_2O_5 because I can then continue to measure it with my radiometer and label the measurements ‘ N_2O_5 ’ without the ‘-like substance’. But the authors do us all a disservice by claiming a positive identification without the proper evidence.

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Toon replies—When we submitted our paper¹ we felt that an additional figure showing the $1,725\text{ cm}^{-1}$ band of N_2O_5 would add little to the paper because of its similarity to the existing figure of the $1,250\text{ cm}^{-1}$ band and because the identification was less clear-cut. I agree with Dr Roscoe that there are strong HNO_3 absorptions in the same spectral region as the $1,725\text{ cm}^{-1}$ N_2O_5 band, but the fact that the N_2O_5 layer peaks at a higher altitude than that of HNO_3 allows the N_2O_5 band to be observed without excessive interference over a narrow range of tangent heights (30–35 km). Figure 1 shows four spectra taken in this tangent-height range, two at sunrise and two at sunset. Because N_2O_5 is almost completely photolysed during the daytime, the sunrise spectra should contain its spectral signature and the sunset spectra should not. Figure 2 shows, superimposed upon the 30.6-km sunrise spectrum, separate calculations of the spectral signatures of N_2O_5 , HNO_3 and O_3 in the same observation geometry. All of these features can be identified in the spectrum; the additional strong, randomly posi-

Fig. 1 Four infrared atmospheric transmittance spectra measured by the ATMOS sensor from 262-km altitude on 30 April 1985 (sunset) and 1 May 1985 (sunrise).

Fig. 2 A superposition of the 30.6-km sunrise spectrum of Fig. 1 and calculated spectra of N_2O_5 , HNO_3 and O_3 offset for clarity. Absorption of all three molecules can be identified in the sunrise spectrum beneath the confusion of strong water-vapour lines.

tioned spectral lines result from water vapour. Although the sunrise–sunset difference of the measured spectra does not conform exactly to the N_2O_5 signature, the wings of the latter being too large, only the most sceptical critic could fail to attribute this difference to N_2O_5 . The calculated spectrum of the $1,725\text{ cm}^{-1}$ N_2O_5 band was based on the room temperature laboratory measurements of Murcray *et al.*², with all spectral lines assumed to have the same ground state energy. Had we given these spectral lines a more realistic temperature dependence, by increasing their ground state energies away from the centre of the band (as Toon *et al.*¹ did for the $1,250\text{ cm}^{-1}$ band) the calculated wings of the $1,725\text{ cm}^{-1}$ band would have been weaker at stratospheric temperatures and their agreement with the measurement perhaps even better. This emphasizes the need for accurate low-temperature, laboratory measurements of both of these N_2O_5 bands so that the untapped information about N_2O_5 contained in the ATMOS spectra can be accurately reduced to volume-mixing-ratio profiles.

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Incubation period for AIDS

SIR—Comments on my article, “The sombre view of AIDS”¹ have been uniformly critical. I would include in this a recent article by Medley *et al.*² on the AIDS (acquired immune deficiency syndrome) incubation period. Nearly all the criticisms focus on the estimation of the