DETECTION AND STRUCTURAL CHARACTERIZATION OF NITROSAMIDE H₂NNO: A CENTRAL INTERMEDIATE IN deNOₓ PROCESSES

MICHAEL C. MCCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; KELVIN LEE, School of Chemistry, UNSW, Sydney, NSW, Australia; JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA.

H₂NNO plays a central role as the initial intermediate in the NH₂ + NO reaction. As the simplest N-nitrosamine, it is also the basis for understanding how specific substituents subtly change the structure of the NNO unit in larger nitrosamines, an important set of compounds that can be produced in foods by nitrites, but which are commonly carcinogenic to humans. Due to its perceived instability, H₂NNO has never been isolated and spectroscopically characterized in the gas phase, but, by means of Fourier transform microwave spectroscopy in combination with millimeter-wave double resonance techniques, the rotational spectrum of the normal and six of its rare isotopic species have been measured to high accuracy between 15 and 90 GHz. For each isotopic species, all three rotational constants have been determined to a fractional accuracy of 10 ppm or better; nitrogen quadrupole coupling constants have also been derived to very high accuracy. By correcting the experimental rotational constants for vibrational corrections calculated theoretically, a precise semi-experimental structure has been derived. These findings are consistent with new CCSD(T) calculations which predict that the equilibrium geometry of H₂NNO is planar, but that it possesses an extremely flat H₂N-X potential, like NH₃. Other aspects of this joint work, including the bond order inferred from the $\epsilon Q q(N)$ coupling constants, and the issue of planarity in substituted derivatives of the form $R₁R₂NNO$, will be discussed.