MICROWAVE SPECTRUM AND STRUCTURE OF A POLAR DIMER OF N2O

NICHOLAS R. WALKER, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.; AN-DREA J. MINEI, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, U.S.A.; and ANTHONY C. LEGON, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..

Cavity Fourier-Transform microwave spectroscopy has been used to characterise a gas phase, polar dimer of N₂O. The polar (N₂O)₂ unit is generated by co-expansion of a gas sample containing a small percentage of N₂O in a helium backing gas. Transitions in the pure rotational spectra of $({}^{15}N_{2}O)_{2}$, $({}^{14}N{}^{15}NO)({}^{15}N_{2}O)$, $({}^{14}N_{2}O)({}^{15}N_{2}O)$ and $({}^{14}N_{2}O)_{2}$ are reported. The measured transitions of $({}^{15}N_{2}O)_{2}$ and $({}^{14}N{}^{15}NO)({}^{15}N_{2}O)$ are assigned and fitted to Hamiltonians allowing rotational, centrifugal distortion and ${}^{14}N$ nuclear quadrupole coupling constants to be determined. Hyperfine structure is assigned for a single $J'_{K'_{-1}K'_{+1}} \rightarrow J''_{K''_{-1}K''_{+1}}$ transition of both isotopomers of $({}^{14}N_{2}O)({}^{15}N_{2}O)$. Nuclear quadrupole coupling constants, χ_{bb} , are reported for all four ${}^{14}N$ nuclei. The measured χ_{bb} are in excellent agreement with those structures predicted from the measured rotational constants. The geometry of the molecule is slipped-parallel. The separation between the central nitrogen nuclei of the monomers in the $r_m^{(1)}$ structure is 3.570(12)Å with the two N₂O monomers respectively oriented 54.69(68)° and 49.85(64)° to the *a*-inertial axis. Simulation of hyperfine structure in the spectrum of the (${}^{14}N_{2}O)_{2}$ isotopomer yields good qualitative agreement with experiment.