FIRST OBSERVATION OF CO TRIMER AND A NEW LOOK AT CO DIMER

M. REZAEI, S. SHEYBANI-DELOUI, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada*; K.H. MICHAELIAN, *Natural Resources Canada, CanmetENERGY, 1 Oil Patch Drive, Suite A202, Devon, AB T9G 1A8, Canada*; A.R.W. McKELLAR, *National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*.

A broad-band (2135 to 2200 cm^{-1}) infrared spectrum is recorded using a tunable quantum cascade laser to probe a supersonic jet expansion of a dilute mixture of carbon monoxide in helium, giving an effective rotational temperature of about 2.5 K. Structure in the region of 2144 cm^{-1} is assigned to the previously elusive CO trimer.[a] In spite of interference from the CO dimer and some remaining unexplained details, there is strong evidence for a planar, cyclic, C-bonded trimer structure, with C_{3h} symmetry and 4.42 Å intermolecular separation, in agreement with theoretical calculations.[b] A modest vibrational blue-shift of +0.85 cm^{-1} is observed for the trimer, as compared to +0.71 cm^{-1} for the C-bonded form of the dimer (and -1.28 cm^{-1} for the O-bonded form).
Analysis of the new dimer spectrum reveals the first known excited state (v_{CO} = 1) levels with A^+ symmetry, and establishes that resonant vibrational splittings are small (<0.2 cm^{-1}) for both the C-bonded and O-bonded dimer isomers. The dimer spectrum extends over a surprisingly large range, with somewhat reduced intensity above 2150 cm^{-1}. A total of 28 new rotational level stacks having A^- symmetry are assigned for v_{CO} = 1 on the basis of combination differences, adding to the 8 stacks previously known,[c] and extending up to 51 cm^{-1} above the v_{CO} = 1 origin. For the first 13 stacks we can establish a correspondence between v_{CO} = 0 and 1, and give labels in terms of values for K, for the low frequency intermolecular geared-bend mode, and for the intramolecular mode (in phase or out of phase C$-$O stretch).

[a] M. Rezaei et al., *J. Chem. Phys.* **138**, 071102 (2013).
[b] G.W.M. Vissers et al., *J. Chem. Phys.* **122**, 054306 (2005); T.A. Ford, *Spectrochim. Acta A* **64**, 1151 (2006).
[c] M.D. Brookes and A.R.W. McKellar, *J. Chem. Phys.* **111**, 7321 (1999); K.A. Walker et al., *J. Chem. Phys.* **113**, 6618 (2000).