

## 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  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$  is assigned to the previously elusive CO trimer.<sup>a</sup> 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.<sup>b</sup> A modest vibrational blue-shift of +0.85  $\text{cm}^{-1}$  is observed for the trimer, as compared to +0.71  $\text{cm}^{-1}$  for the C-bonded form of the dimer (and  $-1.28 \text{ cm}^{-1}$  for the O-bonded form). Analysis of the new dimer spectrum reveals the first known excited state ( $\nu_{CO} = 1$ ) levels with  $A^+$  symmetry, and establishes that resonant vibrational splittings are small ( $<0.2 \text{ cm}^{-1}$ ) 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  $\text{cm}^{-1}$ . A total of 28 new rotational level stacks having  $A^-$  symmetry are assigned for  $\nu_{CO} = 1$  on the basis of combination differences, adding to the 8 stacks previously known,<sup>c</sup> and extending up to 51  $\text{cm}^{-1}$  above the  $\nu_{CO} = 1$  origin. For the first 13 stacks we can establish a correspondence between  $\nu_{CO} = 0$  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).

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<sup>a</sup>M. Rezaei et al., *J. Chem. Phys.* **138**, 071102 (2013).

<sup>b</sup>G.W.M. Vissers et al., *J. Chem. Phys.* **122**, 054306 (2005); T.A. Ford, *Spectrochim. Acta A* **64**, 1151 (2006).

<sup>c</sup>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).