

Infrared spectroscopy of  $(\text{H}_2)_N\text{N}_2\text{O}$  clusters

(岡山大理\*, SIMS, NRC Canada\*\*) ○唐 健\*, A. R. W. McKellar\*\*

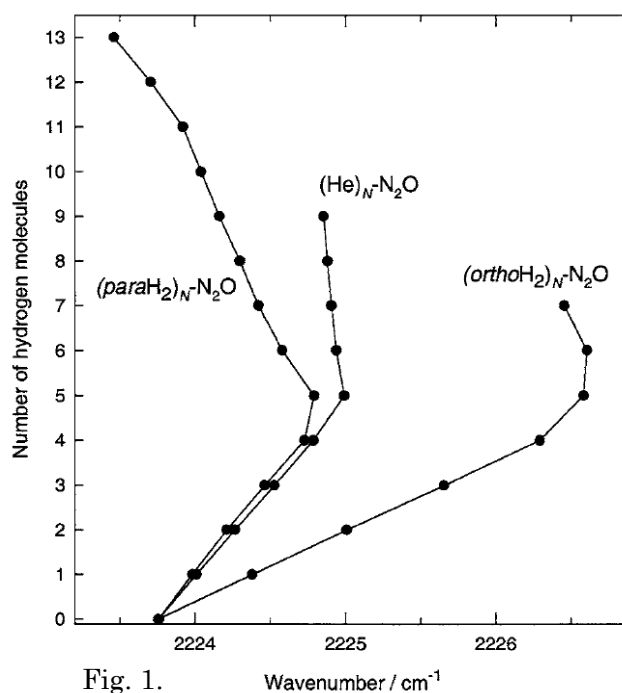
Hydrogen is expected to have superfluidity below its triple point of 13.6 K although helium is the only known matter which shows macroscopic superfluidity. Consequently, macroscopic superfluidity of hydrogen could not be realized with the present technique, but microscopic superfluidity of hydrogen may be realized in cluster size as shown for helium clusters by gas-phase infrared spectroscopy and helium droplet infrared spectroscopy.

Recently, gas-phase infrared spectroscopy of clusters with multi-hydrogen molecules has been studied for  $(\text{H}_2)_N\text{-OCS}$  and  $(\text{H}_2)_N\text{-CO}$  with  $N$  up to 7 and  $N$  up to 14, respectively, in gas-phase. No evidence has been shown for the microscopic superfluidity in these systems. In the present work<sup>(1)</sup>,  $(\text{H}_2)_N\text{-N}_2\text{O}$  clusters for *para*-hydrogen and *ortho*-hydrogen with  $N$  up to 13 are studied by diode-laser infrared spectroscopy in low-temperature supersonic molecular beam.

The  $\nu_1$  fundamental band of  $\text{N}_2\text{O}$  in the  $2225\text{ cm}^{-1}$  region was observed for the  $(\text{H}_2)_N\text{-N}_2\text{O}$  clusters containing *para*- $\text{H}_2$  and/or *ortho*- $\text{H}_2$  and a single  $\text{N}_2\text{O}$  molecule. The pulsed supersonic expansion was probed by a tunable diode laser operating in a rapid-scan signal averaging mode. Slit- and pinhole-shaped orifices were used with a cooled jet nozzle, the slit giving sharper spectral lines and the pinhole giving lower temperatures and more clustering. The nozzle was cooled down to  $-90\text{ }^\circ\text{C}$  with liquid- $\text{N}_2$  flow and the backing pressure of the expansion gas was up to 24 atm. The expansion gas mixture was mostly helium with 1%-3% hydrogen and less than 0.01%  $\text{N}_2\text{O}$ . *Para*- $\text{H}_2$  was prepared in batches by liquefying hydrogen in the presence of a catalyst, in which the residual *ortho*- $\text{H}_2$  impurity level could not be directly measured but is believed to be less than 1%.

The starting point was our previous results for  $\text{H}_2\text{-N}_2\text{O}$  complexes, where the spectral lines of *ortho*- $\text{H}_2\text{-N}_2\text{O}$  appear even though almost pure (>99%) *para*- $\text{H}_2\text{-N}_2\text{O}$  was used. Spectral lines of  $R(0)$ ,  $R(1)$ ,  $R(2)$ ,  $P(1)$ , and  $P(2)$  for  $(\text{para}\text{-H}_2)_N\text{-N}_2\text{O}$  were observed with *para*- $\text{H}_2$  and spectral lines of  $R(0)$ ,  $R(1)$ ,  $R(2)$ ,  $P(1)$ ,  $P(2)$  and a partly resolved  $Q$  branch for  $(\text{ortho}\text{-H}_2)_N\text{-N}_2\text{O}$  were observed with normal  $\text{H}_2$ . Also, mixed  $(\text{para}\text{-H}_2)_N\text{-(ortho}\text{-H}_2)_M\text{-N}_2\text{O}$  clusters were observed with either *para*- $\text{H}_2$  or normal  $\text{H}_2$ .

Vibrational band origins analyzed for the  $(\text{para}\text{-H}_2)_N\text{-N}_2\text{O}$  and  $(\text{ortho}\text{-H}_2)_N\text{-N}_2\text{O}$  clusters were shown in Fig. 1 in comparison

Fig. 1. Wavenumber /  $\text{cm}^{-1}$

with the ones of  $(\text{He})_N\text{-N}_2\text{O}$  clusters obtained previously<sup>(2)</sup>. Vibrational shift turns around  $N=5$  similar to  $(\text{He})_N\text{-N}_2\text{O}$  clusters, which indicates that the first 5 or so  $\text{H}_2$  molecules form a ring around the  $\text{N}_2\text{O}$  similar as the “donut” model in  $(\text{He})_N\text{-N}_2\text{O}$  clusters.

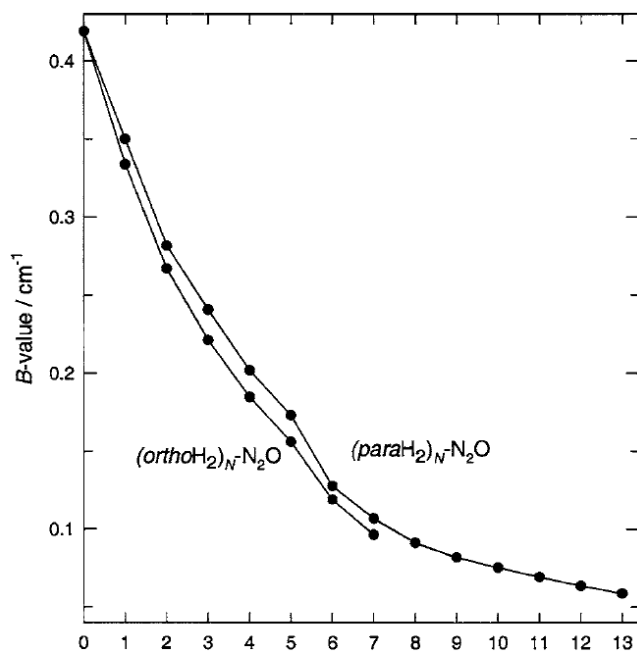


Fig. 2. Number of hydrogen molecules

The most concerned is the variation of the rotational constant with cluster size as shown in Fig. 2. Both  $(para\text{-H}_2)_N\text{-N}_2\text{O}$  and  $(ortho\text{-H}_2)_N\text{-N}_2\text{O}$  clusters show a monotonic decrease in  $B$  in contrast to  $(\text{He})_N\text{-N}_2\text{O}$  clusters, where a turnaround in  $B$  is observed for  $N>6$ . The absence of a turnaround indicates that we have no obvious evidence for superfluid-type behavior for  $(para\text{-H}_2)_N\text{-N}_2\text{O}$  clusters.

Larger  $(para\text{-H}_2)_N\text{-N}_2\text{O}$  clusters up to  $N=15$  or 16 were also observed as shown in Fig. 3. The vibrational shifting stops (or slows down), the regularity of the  $R(0)$  line progressions ends, and the lines begin to broaden. These changes may be related to the

completion of the first solvation shell of  $para\text{-H}_2$  molecules around the  $\text{N}_2\text{O}$ . Another possibility for the confusion

around  $N=15$  could be a manifestation of an onset of superfluid effects. This explanation is supported by the theoretical simulations of  $(para\text{-H}_2)_N\text{-OCS}$  clusters, which show a

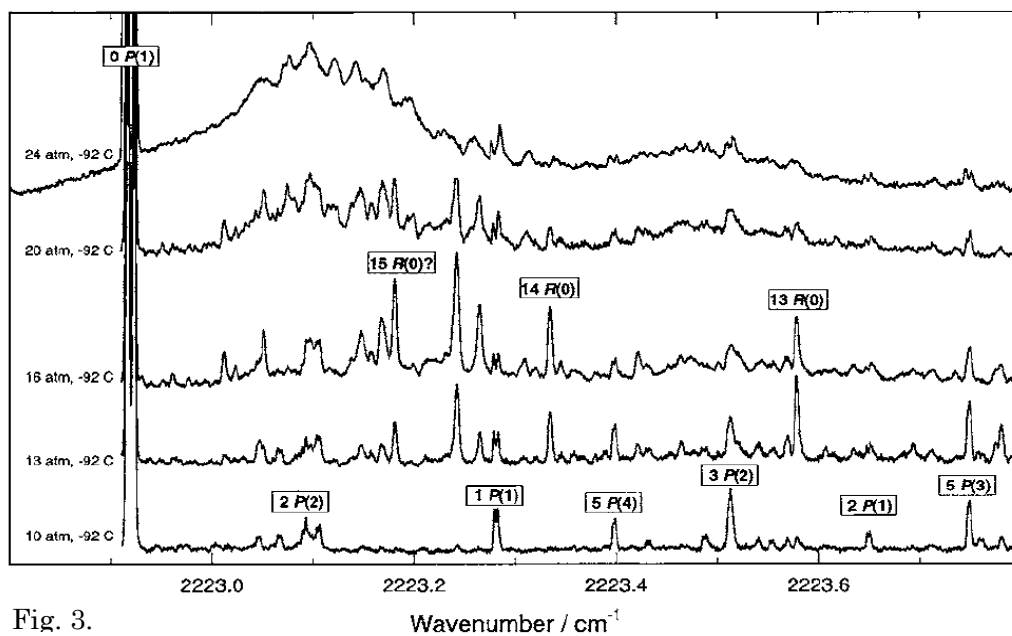


Fig. 3.

generally monotonic decrease in  $B$  value with  $N$  except for a slight bump at  $N=10$  and a larger bump at  $N=14, 15$ .

## References

- (1) J. Tang and A.R.W. McKellar, *J. Chem. Phys.* **123**, 114314 (2005).
- (2) Y. Xu, W. Jäger, J. Tang and A.R.W. McKellar, *Phys. Rev. Lett.* **91**, 163401 (2003).