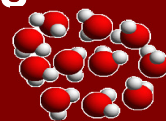


# Electric dipole moments of water clusters from a beam deflection measurement

Ramiro Moro, Roman Rabinovitch, Chunlei Xia, Vitaly Kresin

Department of Physics and Astronomy

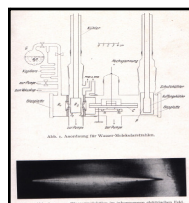
University of Southern California, Los Angeles



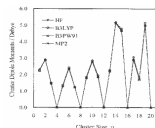
## Background

### WATER CLUSTERS – Discrepancy in the literature

The first – and apparently only – previous deflection experiment with water was done in 1939 on the  $H_2O$  molecule [1]



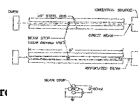
- Theory predicts sizeable electric dipoles for  $(H_2O)_n$  – see, e.g., the result from [2]:



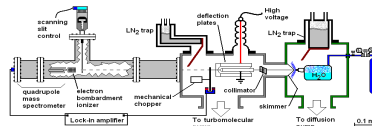
- and VRT spectroscopy has shown a Stark effect for  $(H_2O)_6$  as predicted for a permanent dipole [3]

However

- experiments using the focusing method [4,5] detected no permanent moments for  $n=3-17$ , concluding that all these cluster structures were cyclical and had no net dipoles



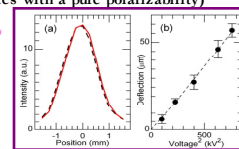
## Experiment



All clusters in the range  $n=3-18$  show only small deflections towards higher electric fields (behaving as particles with a pure polarizability)

Example  $(H_2O)_9$

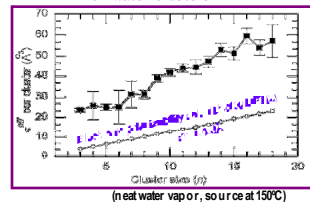
---  $E=0$   
—  $E=79 \text{ kV/cm}$  ( $V=25 \text{ kV}$ )  
Deflection of  $46.1 \pm 5.0 \mu\text{m}$   $\Leftarrow$



(Absolute calibration done with the polarizability of Ar and checked with SF<sub>6</sub>; accuracy is better than 2%)

## Results

### Measured “effective polarizabilities” of water clusters

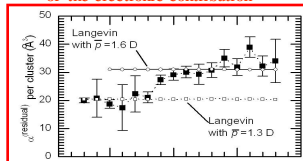


This “polarizability” behavior explains the null result of the focusing experiments mentioned above

But the total “effective” polarizabilities are much higher than the expected electronic contribution

⇒ permanent dipoles masquerade as polarizabilities

### After subtraction of the electronic contribution



## Discussion: Langevin-Debye susceptibility

It has been found [6,7] that “floppy” molecules and clusters (which easily fluctuate between different dipole conformations and orientations) display a statistical response behavior. For “fluxional” water clusters whose molecules move and rotate easily [8], this produces a “reorientational” polarizability

$$\alpha_{\text{effective}} = \alpha_{\text{electronic}} + \frac{\bar{p}^2}{3k_B T}$$

where  $\bar{p}$  is the average magnitude of the fluctuating dipole moment and  $T$  is the internal cluster temperature.

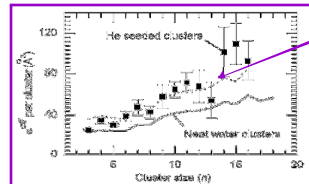
(The magnetic counter part of this behavior has also been observed, e.g. [9,10])

From evaporative ensemble theory [11], the temperature of the water clusters in our experiment is  $T \approx 200 \text{ K}$ . Using this value and the Langevin equation above, we find the values shown in the plot at left.

Note a transition in the population of dipolar structures occurring at  $n=8-9$ , an effect which would be interesting to analyze theoretically.

## Temperature variation of electric response

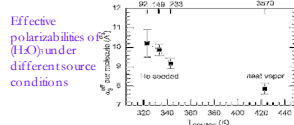
If the above picture is correct,  $\alpha_{\text{effective}}$  should change strongly with the temperature. To verify this, we used helium carrier gas to cool down the beam.



Note: no indication of a cluster freezing transition down to  $\sim 120 \text{ K}$  /in disagreement with molecular dynamics simulations [8] for  $(H_2O)_8$ /

rescaling the neat water expansion data (—) by the Langevin equation to  $T=120 \text{ K}$ .

This temperature is in good agreement with a Stark deflection measurement on a beam of  $H_2O$  molecules [12] and a relaxation calculation [13], confirming the validity of the statistical picture.



## Summary

- ❑ The polarity of  $(H_2O)_{n=3-18}$  clusters has been studied by beam deflection
- ❑ All clusters deflect uniformly, mimicking polarizable behavior
- ❑ The “effective polarizabilities” exceed the electronic component and increase as the clusters are cooled, revealing a large permanent dipole contribution
- ❑ All species access conformations with  $\bar{p} \approx 1.3-1.6 \text{ D}$
- ❑ A shift in the conformer arrangement at  $n=8-9$  is indicated
- ❑ No evidence for freezing down to  $T \sim 120 \text{ K}$
- ❑ A contradiction in the literature concerning water cluster polarity is resolved

## References

- [1] H. Scheffers, Phys. Zeits. **40**, 1 (1939).
- [2] M. Yang *et al.*, Int. J. Quantum Chem. **101**, 535 (2005).
- [3] J. K. Gregory *et al.*, Science **275**, 814 (1997).
- [4] T. R. Dyke, J. S. Muentzer, J. Chem. Phys. **57**, 5011 (1972).
- [5] B. D. Kay, A. W. Castleman, J. Phys. Chem. **89**, 4867 (1985).
- [6] R. Antoine *et al.*, Eur. Phys. J. D **20**, 583 (2002).
- [7] R. Antoine *et al.*, J. Am. Chem. Soc. **124**, 6737 (2002).
- [8] J. Rodriguez *et al.*, J. Chem. Phys. **110**, 9039 (1999).
- [9] M. B. Knickelbein, J. Chem. Phys. **121**, 5281 (2004).
- [10] X. Xu *et al.*, Phys. Rev. Lett. **95**, 237209 (2005).
- [11] C. E. Klots, J. Phys. Chem. **92**, 5864 (1988).
- [12] R. Moro *et al.*, to be published.
- [13] J. Brudermann *et al.*, J. Phys. Chem. A **106**, 453 (2002).