

Electric Dipole Moments of Water Clusters from a Beam Deflection Measurement

Ramiro Moro, Roman Rabinovitch, Chunlei Xia, and Vitaly V. Kresin

Department of Physics and Astronomy, University of Southern California, Los Angeles, California 90089-0484, USA

(Received 19 May 2006; published 18 September 2006)

The response of $(\text{H}_2\text{O})_{n=3-18}$ clusters to an electric field is studied by beam deflection. All clusters deflect uniformly, behaving as polarizable particles. The effective polarizabilities exceed the electronic component and increase as the clusters are cooled, revealing a large permanent dipole contribution. The results resolve a discrepancy concerning the polarity of water clusters and show that all species access conformations with moments exceeding 1 D. The data show no evidence for a freezing transition down to ~ 120 K, but suggest a shift in the conformer arrangement at $n = 8-9$.

DOI: [10.1103/PhysRevLett.97.123401](https://doi.org/10.1103/PhysRevLett.97.123401)

PACS numbers: 36.40.-c, 33.15.Kr, 36.20.Ey

The isolated H_2O molecule is a textbook example of an asymmetric top molecule with a permanent electric dipole moment. An experiment to measure this dipole in a molecular beam was undertaken as early as 1939 [1]. The result was only a qualitative observation of field-induced beam broadening and a rough estimation of ~ 1 D for the dipole magnitude. The rotational Stark effect gives the much more precise value of 1.8546(6) D [2]. It is interesting and instructive to inquire how the dipole moment of water develops from the molecule to the true liquid phase by studying finite clusters. However, despite a large number of theoretical studies, direct experimental information is limited and has discrepancies.

Clusters of n water molecules are generally expected to have finite dipole moments [3,4] (except in particular cases when their geometries make the individual dipoles cancel each other), but an experiment employing beam focusing by a quadrupole electric field found that clusters with $n = 3-6$ had a very weak response [5]. This was interpreted as the species being nonpolar, and it was suggested that all their structures were cyclic, with the protons undergoing out-of-plane motion with a double-well potential. Later work using focusing fields came to the same conclusion for larger clusters, $n = 3-17$ [6], estimating a bound of < 0.05 D for the total dipole moment. On the other hand, a more recent measurement of the vibration-rotational-tunneling Stark effect of cold clusters in a beam gave a dipole moment of ≈ 2 D for the water hexamer [7-9]. Thus there has been inconsistency between the two sets of experimental results, beam deflection and laser spectroscopy.

Work with polar molecules and clusters over the last decade has led to a better understanding of the interpretation of deflection experiments. It has been found that even if the electric dipole moment is strong, its coupling to the cluster vibrations and rotations can lead to a relatively weak paraelectric response. In this case the system mimics the behavior of an object with only an induced polarizability (see [10,11] and references therein). The magnetic counterpart of this behavior has also been observed and

discussed [12-14]. Here we present measurements of the effective electrical polarizabilities of water clusters by deflection in an inhomogeneous electric field, showing that there are indeed significant dipole moments “hidden” behind the small deflections.

The molecular beam machine used in these experiments is outlined in Fig. 1 [15,16]. Water clusters $(\text{H}_2\text{O})_n$ ionized by electron impact are known to appear in the mass spectrum predominantly as protonated cations $(\text{H}_2\text{O})_{n-1}\text{H}^+$ [17,18], with only a small fraction of the clusters in this size range expected to undergo additional evaporation [19]. For a chosen mass peak and deflection voltage, the deflection profile is measured by moving the scanning slit 13 times through the beam in steps of 0.25 mm, alternating voltage on and off passes. With the present setup, beam deflections down to $5 \mu\text{m}$ ($7 \mu\text{rad}$) can be resolved.

Figure 2(a) shows typical profiles. The dashed line depicts the beam without an applied electric field; its width is a consequence of the finite size of the skimmer, collimator, and the scanning slit. The solid line represents the beam intensity under an applied deflecting field. The beam clearly deflects only towards the right, which is the region of the stronger electric field, and there is essentially no broadening (this can be seen, e.g., from the fact that the peak heights are the same). Figure 2(b) shows that the deflection is a linear function of the square of the voltage V applied to the plates. All clusters in the range $n = 3-18$ displayed the same behavior [20].

The linear dependence of the deflection d on V^2 means that the average projection of the cluster dipole moment on the direction of the electric field \vec{E} (call this the x direction) is proportional to the field magnitude, like for a polarizable particle: deflecting force $F_x = p_x(dE/dx) = (\alpha E) \times (dE/dx) = \frac{1}{2} \alpha (dE^2/dx)$. For fixed apparatus geometry, the electric field and its gradient are proportional to V , and the amount of deflection is proportional to the ratio of the transverse velocity, acquired while transiting through the plates, to the forward beam velocity: $d \propto F_x / (nm_{\text{H}_2\text{O}} v^2)$. Here $nm_{\text{H}_2\text{O}}$ is the mass of $(\text{H}_2\text{O})_n$. Incorporating all the geometric quantities into one constant factor

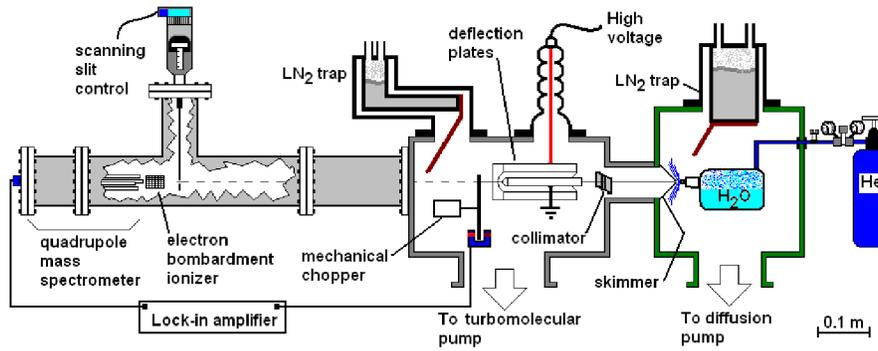


FIG. 1 (color online). An outline of the experimental arrangement. A supersonic beam of water clusters is formed by expanding water vapor, either neat or with helium carrier gas, through a $75 \mu\text{m}$ nozzle. The jet passes through a 0.3 mm skimmer and is collimated by a $0.25 \text{ mm} \times 2.5 \text{ mm}$ slit just before entering the deflecting field region. The inhomogeneous field is created by 152 mm long asymmetric aluminum plates with a “two-wire” cross section and a 2.49 mm gap at the center [15,16]. The deflected clusters travel 709 mm to a 0.25 mm wide slit scanned by a stepper motor (shown rotated by 90° in the figure for clarity), and then enter a quadrupole mass spectrometer (UTI-100, 300 amu range) equipped with an electron-impact ionizer set to 70 eV . Chopping the beam at a frequency of 114.8 Hz and feeding the mass spectrometer output and the chopper pulses into a lock-in amplifier removes the background gas signal as well as determines the cluster speed from the phase difference.

C , one can extract the effective cluster polarizability α_n^{eff} from the deflection via

$$d = \alpha_n^{\text{eff}} C \frac{V^2}{nm_{\text{H}_2\text{O}} v_n^2} \quad (1)$$

Cluster velocities ranged from 1150 m/s for $n = 3$ to 1014 m/s for $n = 18$. Deflections were quantified by Gaussian fits to the profiles of individual slit scans, and error bars were derived from scan-to-scan variations. The geometrical factor C was fixed by calibrating the setup with a supersonic beam of Ar, using its known polarizability of 1.6411 \AA^3 [22]: its average velocity was $523.1(1.2) \text{ m/s}$, and the slope of the d/V^2 line $0.0506(14) \mu\text{m}/(\text{kV}^2)$. To check this calibration, a measurement was done with the symmetric molecule SF_6 ,

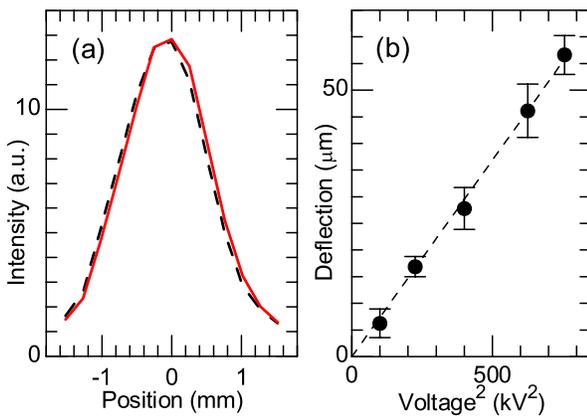


FIG. 2 (color online). (a) Beam profiles of $(\text{H}_2\text{O})_9$ at zero field (dashed line) and with 25 kV on the plates (field of 79.4 kV/cm and a gradient of 375 kV/cm^2 , solid line), yielding a deflection of $46.1 \pm 5.0 \mu\text{m}$. (b) $(\text{H}_2\text{O})_9$ deflections for several plate voltages.

giving a polarizability of 6.69 \AA^3 , only 2.3% higher than the literature value of 6.54 \AA^3 [22]. Additionally, we found the calibration to be in excellent agreement with Stark deflection profiles of the water monomer [21].

The measured effective polarizabilities for clusters prepared by expansion of neat water vapor ($T_{\text{source}} = 423 \text{ K}$, $T_{\text{nozzle}} = 453 \text{ K}$) are plotted as circles in Fig. 4. They range from 7.9 \AA^3 per molecule for the trimer to $\approx 3.2 \text{ \AA}^3$ per molecule for the larger clusters. Additional experiments with heavy water clusters $(\text{D}_2\text{O})_{n=3-16}$ and the same source conditions showed polarizabilities with a similar size dependence, but on average greater by $\approx 13\%$. These α^{eff} values are significantly larger than the expected electronic polarizabilities α^{el} [4,23,24], which are $\approx 1.2 \text{ \AA}^3$ per molecule. It follows that the polarizability-like behavior should in reality be ascribed to an effect of permanent electric dipoles.

As mentioned above, recent work found that such behavior does arise for relatively large polar molecules or clusters which are “floppy,” i.e., undergo internal rotational/vibrational fluctuations, interconverting between different conformations and correspondingly different orientations of their constituent dipoles (as has, in fact, been proposed for water clusters; see, e.g., Ref. [25]). In the statistical limit one expects that during the flight time through the field region the probability of sampling a particular configuration is given by a canonical distribution [26]. The calculation of the effective dipole moment then becomes analogous to the Langevin-Debye theory of orientational polarizability [27]: the projection of the dipole on the field axis is given by $p_x \approx (\bar{p}^2 E_x / 3k_B T)$, where \bar{p} is the average magnitude of the fluctuating-dipole moment and T is the cluster’s internal temperature. Thus the electric field induces a collinear dipole moment, which is then uniformly deflected by the field gradient, instead of being

broadened. This behavior imitates a polarizable particle with an effective polarizability given by a sum of electronic and fluctuating-dipole terms:

$$\alpha^{\text{eff}} \simeq \alpha^{\text{el}} + \bar{p}^2/(3k_B T). \quad (2)$$

A plot of the experimental values presented as $\alpha^{\text{residual}} \equiv \alpha^{\text{eff}} - \alpha^{\text{el}}$ (with α^{el} taken as the B3PW91 density-functional results of Ref. [4]) is shown in Fig. 3.

Behavior according to Eq. (2) explains why the aforementioned refocusing experiments [5,6], performed under similar beam conditions, did not manifest the existence of water cluster dipole moments: the quadrupole arrangement focused only low field seeking clusters, whereas clusters with an “effective polarizability” are all high field seekers. In addition, the thermal factor $(\bar{p}E_x)/(3k_B T)$ reduced the projection p_x to only a small fraction, $<1\%$, of \bar{p} .

This interpretation is also consistent with the fact that the measured response is similar for all clusters, including those even-numbered ones for which the ground state is expected to have no net dipole [3,4,7]: \bar{p} includes averaging over various thermally accessible conformers with different dipole moments, as well as over fluctuations of those dipole moments in time [25].

Water clusters formed in a hot nozzle expansion will cool by evaporation, and evaporative ensemble theory [28] predicts a resultant $T \approx 200$ K. Figure 3 includes a fit to the data using this temperature and Eq. (2). The fit implies $\bar{p} \approx 1.3$ D for $n = 3-8$ and $\bar{p} \approx 1.6$ D for $n = 9-18$, suggesting a transition in the population of dipolar structures at $n = 8-9$ (with a hint of another step at $n = 14$), a finding which would be interesting to analyze theoretically.

If the proposed picture is correct, we should expect α^{eff} to change significantly with temperature. For validation,

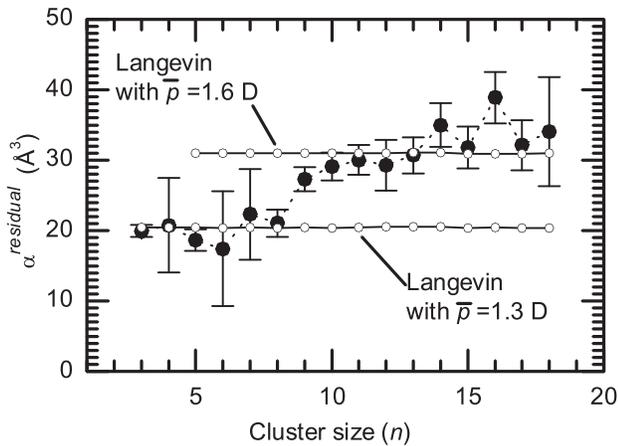


FIG. 3. Solid circles: Measured effective polarizabilities of water clusters (prepared by supersonic expansion of neat water vapor) minus the theoretical electronic contribution $\alpha^{\text{el}} \approx n \times (1.2 \text{ \AA}^3)$ [4]. These residual values are the contribution of permanent dipoles. Dotted line: Langevin formula, Eq. (2), with $T \approx 200$ K. The full effective polarizabilities are shown in Fig. 4.

we used helium carrier gas to cool down the beam in the supersonic expansion, in the spirit of previous work with water clusters [29]. The results are shown in Fig. 4. As expected, they are systematically higher than the values obtained in the neat water case. As shown by the dashed line, the two sets of data can be made to match closely by using Eq. (2) and setting the temperature of the cold beam to $T \approx 120$ K. This fitted value of T agrees well with our Stark deflection measurement on H_2O molecules [21] and is also consistent with a calculation employing a simple relaxation model for our beam parameters [29–31]. The applicability of the statistical picture is therefore confirmed; conversely, the strong temperature dependence of the susceptibility evidences polarity (if the clusters possessed no permanent dipole moments, their electronic and vibrational polarizabilities would not have a $1/T$ behavior [32]).

The fact that the same magnitude of \bar{p} applies in both cases in Fig. 4 implies that all clusters explore their entire relevant conformer landscapes at both temperatures (except possibly the trimer, which, by virtue of its small size, has fewer isomers and also undergoes less cooling collisions with helium atoms). Thus there is no evidence for a freezing transition down to ≈ 120 K [33] (otherwise a strong reduction in the number of populated configurations should occur, accompanied by a significant shift in \bar{p} , especially for those clusters whose ground-state isomers are nonpolar [3,4]), and all the clusters access conformations with sizeable dipole moments.

A qualitative illustration of the same trend over a wider range of carrier gas conditions is shown in Fig. 5 for $(\text{H}_2\text{O})_3$: as the water partial pressure is reduced, promoting

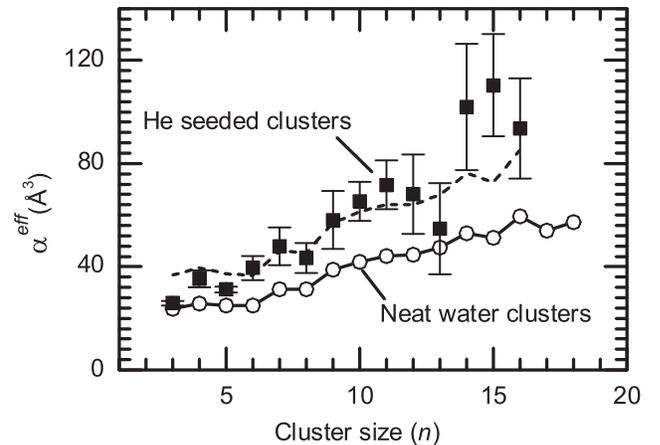


FIG. 4. Squares: Effective polarizabilities of cooled water clusters prepared by expanding a mixture of helium and water vapor into vacuum ($P_{\text{He}} = 670$ Torr, $T_{\text{source}} = 343$ K, $P_{\text{H}_2\text{O}} = 233$ Torr, $T_{\text{nozzle}} = 353$ K). Circles: Full effective polarizabilities for the hotter clusters (from which Fig. 3, which includes the error bars, was derived). Dashed line: rescaling of the latter values using Eq. (2) with $T = 120$ K.

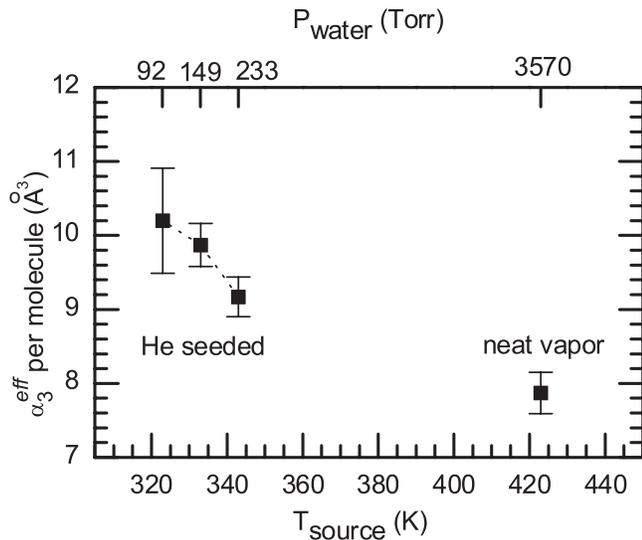


FIG. 5. Effective polarizabilities of $(\text{H}_2\text{O})_3$ under different source conditions. For the seeded expansion, P_{He} was kept at 670 Torr and the water vapor pressure varied. The data point for neat vapor expansion is also shown.

stronger cooling in the expansion, the deflection response is enhanced.

In summary, we have employed the technique of electric field deflection to gain insight into the polarity of water clusters as a function of their size and temperature. All clusters in the investigated size range behaved as polarizable particles, but the high values of the effective polarizabilities and their strong temperature dependence revealed a dominant contribution of the permanent electric dipole moments, present for all clusters. These moments correspond to a canonical average of the thermally sampled cluster conformations and suggest a transition from $\bar{p} \approx 1.3$ D to $\bar{p} \approx 1.6$ D at $n = 3-8$ (and possibly another transition at $n = 14$). No evidence for cluster freezing down to $T \approx 120$ K has been observed, but it will be interesting to extend the measurements to lower temperatures in order to search for such a transition and to explore the limits of the efficacy of the statistical Langevin-Debye description of cluster response.

We appreciate helpful discussions with Dr. U. Buck and Dr. Ph. Dugourd. This work was supported by the NSF.

- [1] H. Scheffers, *Phys. Z.* **40**, 1 (1939).
 [2] S. A. Clough *et al.*, *J. Chem. Phys.* **59**, 2254 (1973).
 [3] H. Kabrede and R. Hentschke, *J. Phys. Chem. B* **107**, 3914 (2003).

- [4] M. Yang, P. Senet, and C. Van Alsenoy, *Int. J. Quantum Chem.* **101**, 535 (2005).
 [5] T. R. Dyke and J. S. Muentzer, *J. Chem. Phys.* **57**, 5011 (1972).
 [6] B. D. Kay and A. W. Castleman, Jr., *J. Phys. Chem.* **89**, 4867 (1985).
 [7] J. K. Gregory *et al.*, *Science* **275**, 814 (1997).
 [8] K. Liu, M. G. Brown, and R. J. Saykally, *J. Phys. Chem. A* **101**, 8995 (1997).
 [9] No Stark effect was detected for $n = 3-5$. The tetramer was not expected to have a dipole moment in the ground state, and the absence of the Stark effect in the trimer and pentamer was interpreted as a zero-average effect caused by the facile flipping of the dipole moment through the plane of the cluster due to a low energy barrier.
 [10] M. Broyer *et al.*, *C.R. Physique* **3**, 301 (2002).
 [11] M. Abd El Rahim *et al.*, *J. Phys. Chem. A* **109**, 8507 (2005).
 [12] W. A. de Heer, P. Milani, and A. Châtelain, *Phys. Rev. Lett.* **65**, 488 (1990).
 [13] M. B. Knickelbein, *J. Chem. Phys.* **121**, 5281 (2004).
 [14] X. Xu *et al.*, *Phys. Rev. Lett.* **95**, 237209 (2005).
 [15] K. Clemenger, Ph.D. thesis, University of California, Berkeley, 1985.
 [16] G. Tikhonov *et al.*, *Rev. Sci. Instrum.* **73**, 1204 (2002).
 [17] C. E. Klots and R. N. Compton, *J. Chem. Phys.* **69**, 1644 (1978).
 [18] B. D. Kay, Ph.D. thesis, University of Colorado at Boulder, 1982.
 [19] U. Buck and M. Winter, *Z. Phys. D* **31**, 291 (1994).
 [20] Only the monomer and the dimer had more complicated profiles, which will be discussed elsewhere [21].
 [21] R. Moro *et al.* (to be published).
 [22] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boca Raton, 2001), 82nd ed.
 [23] L. Jensen *et al.*, *J. Chem. Phys.* **117**, 3316 (2002).
 [24] T. K. Ghanty and S. K. Ghosh, *J. Chem. Phys.* **118**, 8547 (2003).
 [25] J. Rodriguez *et al.*, *J. Chem. Phys.* **110**, 9039 (1999).
 [26] R. Antoine *et al.*, *Eur. Phys. J. D* **20**, 583 (2002); *J. Am. Chem. Soc.* **124**, 6737 (2002).
 [27] M. A. Omar, *Elementary Solid State Physics* (Addison-Wesley, Reading, 1993).
 [28] C. E. Klots, *J. Phys. Chem.* **92**, 5864 (1988).
 [29] J. Brudermann, U. Buck, and V. Buch, *J. Phys. Chem. A* **106**, 453 (2002).
 [30] D. R. Miller, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, New York, 1988), Vol. 1.
 [31] H. Pauly, *Atom, Molecule, and Cluster Beams* (Springer, Berlin, 2000), Vol. 1.
 [32] I. Compagnon *et al.*, *Phys. Rev. Lett.* **89**, 253001 (2002).
 [33] This conclusion is in disagreement with the molecular dynamics simulations of Ref. [25] for $(\text{H}_2\text{O})_8$.