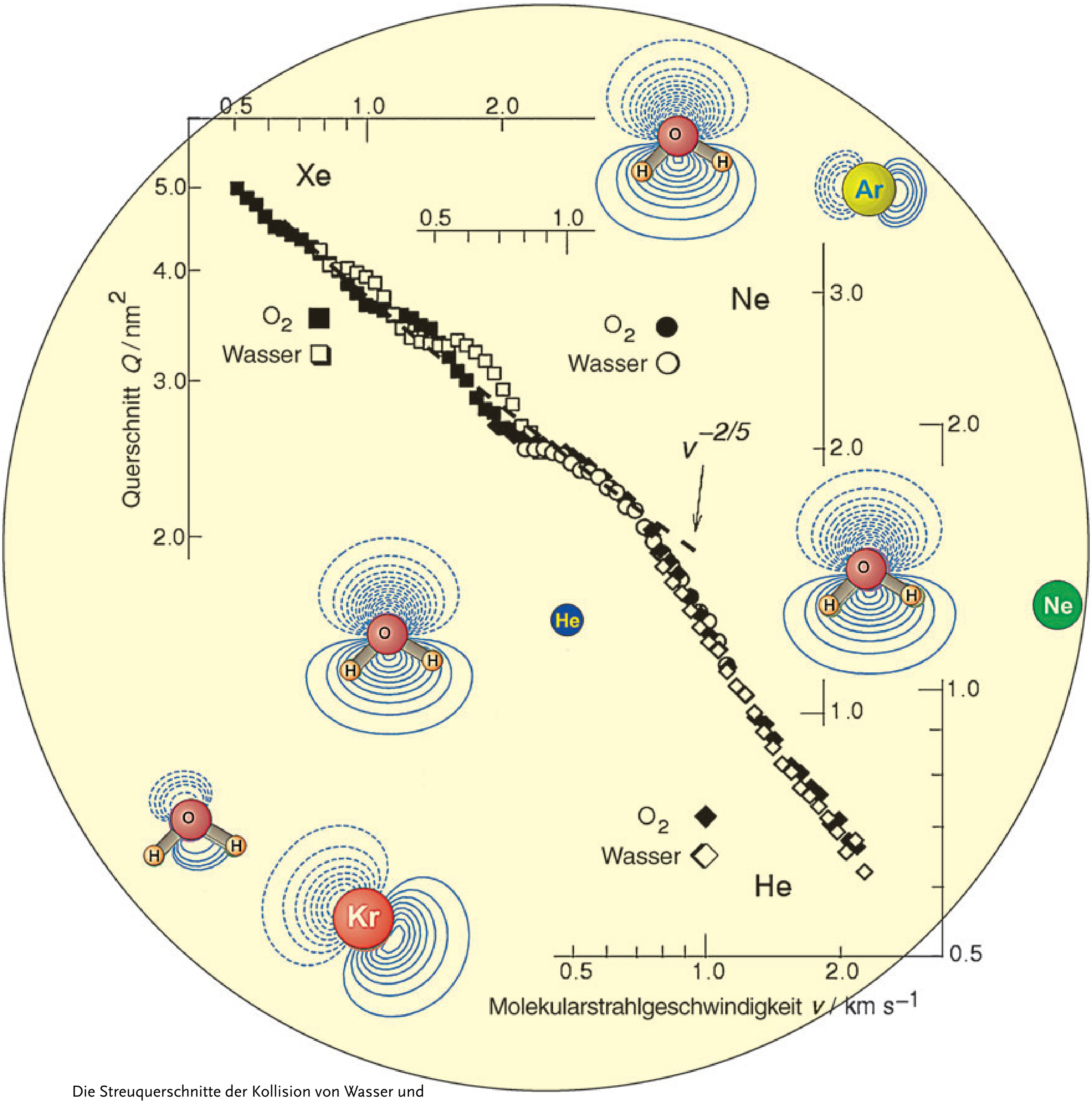
Zuschriften



Die Streuquerschnitte der Kollision von Wasser und Sauerstoff mit den fünf Edelgasen enthüllen den Beginn von H-Brückenbindungen in Wasser-Edelgas-Komplexen, deren Stärke von He bis Xe zunimmt. Einzelheiten über die Bestimmung der Stärke der Wechselwirkung, die über reine Van-der-Waals-Kräfte hinausgeht, finden sich in der Zuschrift von D. Cappelletti et al. auf den folgenden Seiten.

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Hydrogen Bonds

Glory-Scattering Measurement of Water–Noble-Gas Interactions: The Birth of the Hydrogen Bond**

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Herein we describe molecular-beam scattering experiments probing the interactions of water with He, Ne, Ar, Kr, and Xe, the observation of the quantum mechanical "glory" interference effect, and the determination of well depths, well positions, and strengths of long-range attraction. Comparisons with expectations from features of typical van der Waals (vdW) dimers indicate how a trend develops along the series for water to bind more strongly than for pure vdW, by means of state-of-the-art ab initio calculations, in which a proton is protruded as a binding bridge towards the heavier noble gases. These precise measurements of the manifestation of an embryonic hydrogen bond contribute to the understanding of this ubiquitous phenomenon and offer important insight for its modeling.

Intermolecular noncovalent interactions control myriad phenomena.[1] They arise from the critical balance of several components, such as electrostatics, induction, and dispersion, which operate at long range, and overlap (size repulsion and charge-transfer), which act at short range.[2] Among intermolecular noncovalent interactions those involving water[3] are of paramount relevance as the archetype of polar hydrogen-containing molecules. They are crucial for the description of its liquid state, its properties as a solvent, and its aggregates. Manifestations and properties of the hydrogen bond have been intensively studied over three quarters of a century, and are currently under more scrutiny than ever, as the list of basic open questions is still impressive.[3,4] Characterizing the relative importance of the various components of the overall noncovalent interaction and understanding how their features modify as different systems are considered are important tasks: the modeling of the diverse components in terms of monomer properties requires appropriate combinations and extensions of experimental and theoretical information on prototypical aggregates. The paradigmatic example is again the most studied liquid, that is, water,[3] which has been simulated by a variety of interaction potential models, often involving only descriptions of electrostatic and size-repulsion components: when calibrated on the gas-phase dimer, that is, on the water–water interaction, the success of these models in accounting for properties of the liquid is only partial.

Herein we focus on the simplest aggregates, those of water with the five noble gases, for which contributions to the interaction from the electrostatic component are absent, and the remaining ones are hopefully amenable to proper testing and modeling. The question is whether the simple vdW picture[2] suffices, or whether there is more to it. The lighter systems, particularly that of He, have been the target of numerous theoretical investigations;[5–7] the heavier ones (that of Kr and Xe) are practically unknown. Except for He[8] and Ar,[9] accurate experimental characterizations are missing. We show that the systematic investigation of the five water–noble-gas systems, the study of variations of our observables along the series, and comparison with the behavior of analogous systems, prototypical of vdW, provide unique information on the strength and range of intermolecular forces and cast light on the nature and role of interaction components which add to the vdW forces.

This series of collisional experiments was carried out in an apparatus (see Figure 1 and details in references [10,11]) in

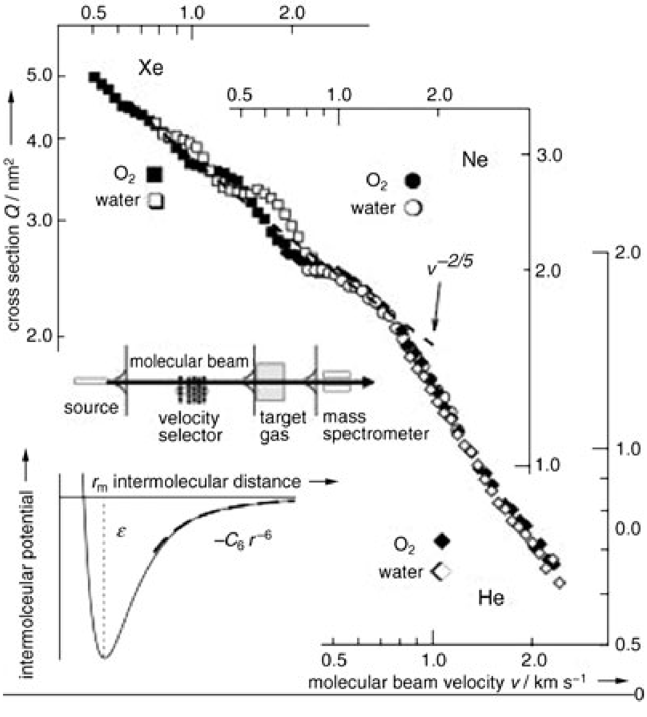

Figure 1. Direct probe of intermolecular interactions. For details, see the Experimental Section. The measurement of the beam attenuation provides $Q(v)$, which is a direct probe of the intermolecular potential features r_m, ε, and C_6 (see text). Typical data can be displayed against molecular beam velocity v on a universal log–log plot, which allows proper scaling to exhibit the coincidence in $Q(v)$ for the Ne and He data, in contrast with the nearly antiphase "glory" behavior for Xe, which is the notable difference visible here between water and oxygen systems (see Figure 2).

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which a well-collimated and velocity-selected "hot" molecular beam of water[12] is scattered by a noble-gas target. The combined use of high angular and velocity resolution permits the total quantum cross section Q to be measured over an ample range of the beam velocity υ.[12] The $Q(\upsilon)$ results show:

1) The characteristic average decrease as $\upsilon^{-2/5}$ (see Figure 1, Figure 2), which provides information on the coefficient C_6 of the leading term of the attraction at long range.

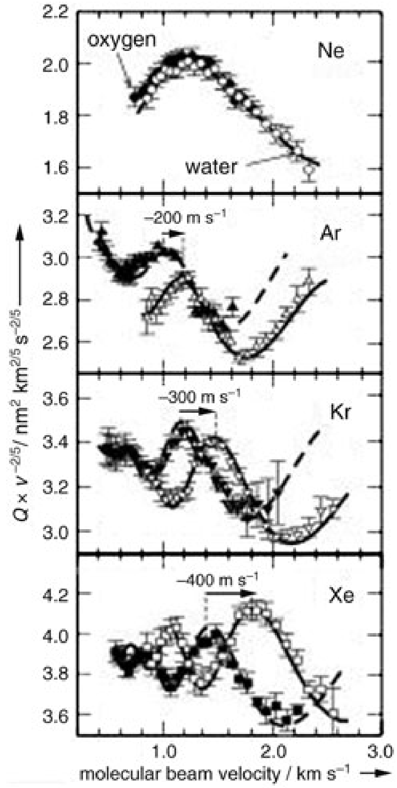


Figure 2. Cross sections (multiplied by $\upsilon^{2/5}$ to emphasize the glory oscillations) as a function of υ for collisions of water and O_2 with Ne, Ar, Kr, and Xe (filled and open symbols, respectively); continuous and dashed curves are corresponding fits with the potential parameters ε, r_m, and C_6 of Table 1; glory shifts are indicated by arrows.

2) The manifestation of an oscillatory pattern, the "glory" interference effect, superimposed on the smooth component, whose frequency and amplitude correlate with depth ε and position r_m of the potential well.
3) The steeper falloff of Q as a function of υ in water–He, which suggests that attraction and repulsion simultaneously influence the scattering in the energy probed by the present experiments.[12]

Illuminating is the direct comparison in Figures 1 and 2 with results from analogous experiments on molecular-oxygen–noble-gas-atom systems: in such well-established series of partners (prototypical vdW interactions[2]), both the long- and medium-range behaviors can be compared with those of the water systems in view of the similarity of oxygen and water in terms of molecular polarizability—the basic property for scaling vdW forces in the full distance range.[13–15] Characteristic potential parameters extracted from the analysis are listed in Table 1.

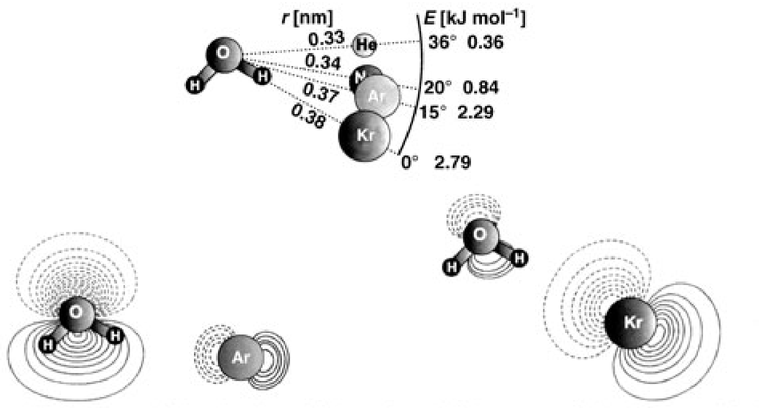
We have thus provided an accurate determination of the spherically averaged interaction, the leading term in its multipolar expansion. For water–He and water–Ar systems, there is full agreement with previous differential scattering[8] and spectroscopic determination,[9] respectively. In detail: 1) For the lighter gases, He and Ne, the coincidence of cross sections for the water and the oxygen systems suggests that a vdW interaction is also operative in the water case; indeed, the involved components[2] (repulsion, dispersion, induction) can be modeled on the polarizabilities of the partners.[13–15] 2) As we move to the heavier members of the series, the average components of the water cross sections still coincide with those of the oxygen systems and continue to be in accord with polarizability-based models of vdW interactions,[13–15] but this is not so for the "glory" features, which are very sensitive to the depth and position of the wells. The progressive glory shift towards higher velocities on going towards Xe (see Figure 2) is thus a precise measure of an increasing binding strength, larger than expected for pure vdW forces (see Table 1).

Table 1: Potential parameters of the isotropic interaction for water–noble-gas and for molecular oxygen–noble-gas systems. vdW predictions, obtained by combining[14,15] size repulsion with dispersion plus induction attraction, are also reported. The equilibrium distance is defined with respect to the center of mass of the water molecule.

	ε [kJ mol^{-1}]	r_m [nm]	C_6 [10^{-4} kJ nm^6 mol^{-1}]	Refs.
water–He	0.265	0.345	6.3	this work
	0.273	0.342	6.1	predicted
oxygen–He	0.241	0.350	7.4	[17,18]
water–Ne	0.550	0.350	13.7	this work
	0.546	0.346	13.0	predicted
oxygen–Ne	0.557	0.350	14.5	[17]
water–Ar	1.39	0.363	42.9	this work
	1.13	0.374	42.5	predicted
oxygen–Ar	1.11	0.372	48.8	[17,19]
water–Kr	1.65	0.375	63.7	this work
	1.37	0.386	62.9	predicted
oxygen–Kr	1.29	0.388	68.0	[10]
water–Xe	1.92	0.393	102	this work
	1.55	0.404	93.7	predicted
oxygen–Xe	1.47	0.405	98.4	[10]

We believe that such an increase in well depths is the manifestation of a short-range reinforcing attractive component to the bond and its role amplifies as distance decreases (as typical of a covalent or charge-transfer contribution): moving towards Xe along the series of noble gases, ionization potentials decrease, proton affinities increase, and there is circumstantial evidence for sharing of external electrons between the partners in the complexes. We looked for confirmation of such a picture and for further insight by extensive state-of-the-art quantum chemical calculations.[16]

They are in a sense complementary here, because although quantum chemistry encounters well-known difficulties with absolute estimations of the bond energies of intermolecular forces, its use is of value in searching for the geometries of most stable structures, while our experiments probe absolute orientational averages. The search was made as the noble gas moves in the plane of the water molecule, and Figure 3 shows that progressive alignment along the O−H bond is found when heavier noble gases are considered. Such an alignment is known as one of the signatures of the hydrogen bond,[20] while vdW considerations predict a sideways approach, that is, along the direction of minimum electron density in water (see the helium case). An insurgence of covalence is observed in the density maps of hybrid orbitals in the cases of Ar and Kr (Figure 3; the Xe case is currently too hard to study, as it requires a relativistic treatment).



second highest occupied molecular orbital

fourth highest occupied molecular orbital

Figure 3. Picture of water–noble gas interactions from ab initio (MRCI) calculations.[16] Oxygen-atom–noble-gas distances *r*, bond angles, and binding energies *E* are given for the most stable configuration of each water–noble-gas complex. The analysis of orbitals corresponding to all structures gave complete separations between those of water and those of the noble gas for He and Ne, although geometries vary. For Ar and Kr, orbitals showing incipient covalence due to charge-sharing appear: for Ar, the hybrid of the figure involves a π_y orbital of the noble gas (coplanar with water) and the bond orbital of OH (σ, π_x, π_y of O and σ of H); it is the second highest occupied molecular orbital. Also in Kr–water an orbital which contains contributions of the noble gas and water is found; it is the fourth highest occupied molecular orbital, which is formed by the π_y orbital of krypton and the σ orbital of hydrogen. In this case the noble gas appears to preferentially interact with just one of the hydrogen atoms of water, as confirmed by the geometry of the complex.

The relevance of the effect can be discussed quantitatively: Taking Kr as the study case for comparison of theory and experiment, we see that the binding energy (Figure 3) is about 1 kJ mol^{-1} higher than $\varepsilon = 1.65$ kJ mol^{-1}, which can be compared with the expected value of 1.37 kJ mol^{-1} for pure vdW interactions (Table 1). The magnitude of the binding energy for Kr and Xe is therefore in the range of the so-called weak hydrogen bonds[21,22] (strong hydrogen bonds can be up to an order of magnitude stronger), and it is important to stress that only a fraction (ca. 50 % for Kr) is accounted for by vdW forces.

This conclusion establishes how components of different nature contribute to a noncovalent interaction, specifically to a simple case study of noncovalent interactions. This type of information is of interest for modeling these interactions to understand the structure and assist in the formulation of the molecular dynamics for the enormous variety of phenomena in which the hydrogen bond plays a major role. Extensions of these measurements to systems consisting of water and simple molecules are in progress.

The two systems water–helium and water–argon can be considered as best characterized, also with regard to potential anisotropies. This information opens perspectives for producing and analyzing collisional alignment phenomena in supersonic seeded molecular beams of water. This should be in line with our previous work with diatomic molecules,[23–25] benzene,[26,27] and C_2 hydrocarbons,[28] and would provide the ground for extending this type of measurements[10] to also probe anisotropy effects in the interactions of water.

Experimental Section

In the experimental apparatus for the measurement of total scattering cross sections *Q* (see Figure 1), the water (or molecular oxygen) beam emerging from a nearly effusive source is detected by a quadrupole mass spectrometer.[12] Along a path of about 2 m the beam is collimated by a series of skimmers and defining slits, velocity-selected by a set of rotating slotted disks with a resolution of about 5 % (fwhm), and "attenuated" by the noble-gas target, which is confined in a scattering chamber, cooled to about 90 K to minimize effects of gas random motion.

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[12] The source nozzle is heated to about 600 K to avoid cluster formation[8] and to ensure that rotational excitation is large enough that spherically averaged water interactions are probed. In most experiments, heavy water (100% isotopically pure D_2O) was used to take advantage of the much lower background noise at mass 20 rather than at 18 in the detector. The experimental range of beam velocities (0.8–2.5 $km\,s^{-1}$) corresponds to collision energy ranges of 6–56 $kJ\,mol^{-1}$ for water and 10–70 $kJ\,mol^{-1}$ for molecular oxygen.

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[15] Semiempirical evaluation[13,14] using atomic and molecular polarizabilities and the permanent dipole moment of water suggests that under the present experimental conditions, which involve water at high rotational temperature, the C_6 coefficient is accounted for to more than 90% by dispersion forces (induced dipole/induced dipole), while induction contributions (included in the present analysis and due to permanent dipole/induced dipole) play a minor role.

[16] CCSD(T) and MRCI calculations were carried out to determine both energy and structure of the water–noble-gas systems (from He to Kr) in the neighborhood of the absolute minimum in the intermolecular interaction potential energy. The ab initio CCSD(T) method was used with several basis sets: cc-VDZ, cc-VTZ, and their augmented versions aug-cc-VDZ and aug-cc-VTZ. All geometries were optimized by using analytical gradient procedures. All structures reported correspond to fully converged geometries with gradients and displacements below the standard thresholds implemented in Gaussian 98. The multireference method MRCI was used with the aug-cc-VTZ basis set. An ample set of about 600 single potential-energy points on each surface was analyzed. Partial charges and orbital occupations, based on the natural bond orbital (NBO) scheme and partly on Mulliken analysis, have been also taken into account to cast light on the nature of the water–noble-gas interactions.

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