We report a joint experimental and theoretical study that directly tests the quality of the potential energy surfaces used to calculate energy changing cross sections of water in collision with helium and molecular hydrogen, at conditions relevant for astrophysics. Fully state-to-state differential cross sections are measured for H$_2$O–He and H$_2$O–H$_2$ collisions at 429 and 575 cm$^{-1}$ collision energy, respectively. We compare these differential cross sections with theoretical ones for H$_2$O+H being derived from state-of-the-art potential energy surfaces [P. Valiron et al., J. Chem. Phys. 129, 134306 (2008)] and quantum scattering calculations. This detailed comparison forms a stringent test of the validity of astrophysics calculations for energy changing rates in water. The agreement between theory and experiment is striking for most of the state-to-state differential cross sections measured. © 2010 American Institute of Physics. [doi:10.1063/1.3475517]
externally cooled by cold N2 gas to a temperature of 170 K in order to
an iron oxide catalyst at 20 K and was then expanded through a pulsed valve
rotational states of H2. Hence, an important difference be-
to 170 K
forward direction. Forward scattering is thus favored for
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ortho-para symmetry. 6

Images collected with the H2O and H2 or He beam sepa-
rated in time were subtracted from images collected in opti-
mal time overlap for background correction. A set of
background-corrected images is shown in Fig. 2(b). These
images are density maps of nascent H2O; conversion to the
desired flux map is carried out using the IMSIM software
procedure, 13,14 which reproduces a simulated density image
in quantitative agreement with the raw images. The derived
flux angular distributions (DCSs, dσ/dθ) for the selected im-
geous are shown as black lines in the panels of Fig. 3.

An important experimental observation is that for the
same final states at nearly the same collision energy, water
scatters much more strongly in the forward direction (defined in Fig. 2)
due to collisions with H2 compared to He. Changing
the H2 supersonic beam conditions (using para-H2 versus
normal-H2 and cooling the H2 nozzle assembly from ~330
to 170 K), we find that the scattering remains strongly
in the forward direction. Forward scattering is thus favored for all
rotational states of H2. Hence, an important difference be-
tween H2 and He is indicated in our differential measure-
ments, even when scattering is for the most part by
para-H2(J=0), which is often assumed to behave similarly to
He.15

The experimental data are compared here with DCS pre-
dictions from a fully quantum analysis using the most recent
and advanced PES for the nonreactive systems H2O+He (Ref. 16)
and H2O+H2. 17,18 Few such calculations exist in
literature. 1,19 For the H2O+H2 case, a full nine-dimensional
PES (including all inter- and intramolecular degrees of free-
don) was obtained from Ref. 18. This nine-dimensional PES
was averaged over the vibrational ground state wave func-
tions of H2O and H2, yielding a five-dimensional rigid-body
PES. This latter PES has been used to calculate many energy
changing cross sections and rates relevant for astrophysics, 20-22
making it all the more important to per-
form the present evaluation. The H2O–He PES was derived from
the PES of Hodges et al. 16 using their routines as input
to our fitting scheme, which is similar to the original scheme
of Green et al.23

The scattering S-matrices needed for computing DCSs
for both H2O–H2 and H2O–He were calculated by employ-
ing the close coupling formalism implemented in the
MOLSCAT program. 24 For H2 with J=1,2, the DCS calcu-
lation made use of an algorithm derived from the original DCS
formulas. 25 Inelastic cross sections of interest were con-
verted to 1%. For the specific angles 90°, 135°, and 180° in the DCS plotted in Fig. 3. The lower left diagonal arrow shows the
propagation direction of the ionization laser beam. (b) Background sub-
tracted images of inelastically scattered H2O in the indicated final Jk,kv state for collisions with para-H2 and He.

FIG. 1. Schematic of the crossed-beam VMI apparatus. Pulsed molecular
beam expansions of pure H2 or He and H2O in Ar are skimmed and crossed
at 90°. Newly formed rotationally excited H2O is state selectively ionized by
a pulsed laser operating around 248 nm. The H2O+ ions are projected by a
VMI lens to a two-dimensional imaging detector monitored by a charge
coupled device (CCD) camera. Normal H2 was converted to para-H2 using
an iron oxide catalyst at 20 K and was then expanded through a pulsed valve
eexternally cooled by cold N2 gas to a temperature of 170 K in order to
decrease the population of H2(J=2).

FIG. 2. (a) Raw image of H2O in the (Jk,kv = 10) final state created by
scattering of H2O(10j) with helium. A color bar on the left side shows the
linear intensity scale for the signal. Three signals are seen; a trace amount of
water in the He beam (vHe, vertical direction), the residual (~5%) populat-
on of H2O(10j) in the water beam (vH2O, horizontal direction), and the
two-dimensional projection of the three-dimensional Newton sphere moving
at the center of mass velocity (vCM). The dashed circle indicates the size of
the Newton sphere for elastic scattering and the directions described as
forward, side, and backscattering in the center-of-mass frame (0°, 90°, and
180° in the DCS plotted in Fig. 3). The lower left diagonal arrow shows the
propagation direction of the ionization laser beam. (b) Background sub-
tracted images of inelastically scattered H2O in the indicated final Jk,kv state for collisions with para-H2 and He.
and final states. In this calculation, the coupled channel treatment includes a full description of molecular $\text{H}_2$, including its anisotropy, but the partial wave sum used for construction of the DCS assumes a rotor basis, that is, when $\text{H}_2$ was treated as an atom in the rotor basis as before, but considering only $J=0$ as initial and final states (see text). Scattering angle (deg), $x$-axes; DCS in arbitrary units, all normalized to unity, $y$-axes. Scattering energies: $\text{H}_2\text{O}–\text{H}_2, 575 \text{ cm}^{-1}; \text{H}_2\text{O}–\text{He}, 429 \text{ cm}^{-1}$. Experimental signal in the region of $0^\circ–10^\circ$ is not reliable due to background subtraction uncertainty.

For the sake of comparisons between $\text{He}$ and $\text{para-H}_2$ scattering, we also show computed DCSs for scattering between water and $\text{para-H}_2$ using the $\text{H}_2$ $J=0,2$ rotor states in the channel basis as before, but considering only $J=0$ initial and final states. In this calculation, the coupled channel propagation used for computation of the $S$ matrix elements includes a full description of molecular $\text{H}_2$, including its anisotropy, but the partial wave sum used for construction of the DCS from the $S$ matrix elements is identical to that for $\text{H}_2–\text{H}_2$ collisions. The results are shown as blue lines in the left panels of Fig. 3. In this case, the DCS structure becomes very different from the results that include an average over the experimental rotational state distribution. The strong forward scattering disappears and the overall structure becomes qualitatively similar to scattering of $\text{H}_2\text{O}$ by $\text{He}$. Very similar results were obtained when only $J=0$ was included in the $\text{H}_2$ rotor basis, that is, when $\text{H}_2$ was treated as an atom in the scattering calculation. Apparently the most important difference between scattering by $\text{He}$ and by $\text{H}_2$ ($J=0$) is the different shape of the potential; in particular, the well is deeper for $\text{H}_2$. While no attempt is given here to compare absolute values of cross sections, the computed DCSs for $\text{He}$ and for $\text{H}_2$ ($J=0\rightarrow0$) show strong similarities at the energies studied, away from the resonance regimes.

$\text{H}_2\text{O}–\text{H}_2$ scattering is thus quite sensitive to the initial rotational state of the $\text{H}_2$, even though most collisions result in no change in its rotational state. Ignoring this dependence and treating all $\text{H}_2$ molecules as $J=0$ molecules or as atoms can introduce important errors. The common procedure of estimating rates for $\text{para-H}_2$ collisions with those from simpler $\text{He}$ calculations should thus be applied with caution.

Differences in the scattering of water by $\text{para-H}_2$ and normal-$\text{H}_2$ have been found in pressure broadening experiments and simulations at $50<\text{T}<200$ K.\[^{28,29}\] The present experiments, however, did not detect a qualitative change in the DCS changes in $\text{H}_2$ beam conditions. In our experiment, it is not possible to produce a beam of pure $\text{para-H}_2$ ($J=0$). Even at the nozzle temperature of 170 K, the expected population ratio of $\text{para-H}_2$ ($J=0$) to $\text{para-H}_2$ ($J=2$) is still 4.3:1. Replacing normal-$\text{H}_2$ by $\text{para-H}_2$ at this temperature in our apparatus produced beams with measured $\text{H}_2$ populations in $J>0$ states of 28%, and the observed images had quite similar angular distributions to those observed under other beam conditions. It is likely that this state distribution was not pure enough to reveal the $\text{He}$-like DCS predicted by the calculation. These experimental indications are qualitative for the present apparatus configuration because the reliability of the signal in the forward scattering region suffers from wide beam angles and background subtraction uncertainty. Improved experiments with more narrow beams and a higher accuracy in the forward scattering region, and more detailed comparisons with scattering by the other rare gases as well as by $D_2$ (whose spin statistics are inverted with respect to $\text{H}_2$) are under way. Lower collision energies will also be studied using a smaller molecular beam crossing angle.

In summary, experiments are now possible that provide sensitive information in the form of state-to-state differential cross sections for collisions of $\text{H}_2\text{O}$ with $\text{H}_2$, $\text{He}$, and other species under conditions relevant to those of interstellar space. Although the center-of-mass energy tested here is somewhat higher than the usual energies found in interstellar matter, the shape of the PES has been thoroughly tested, setting great confidence in the calculating scheme that we used to obtain the PES. The measured and calculated properties for the most part agree quite well, giving confidence in the quality of the PESs describing the $\text{H}_2\text{O}–\text{H}_2$ and $\text{H}_2\text{O}–\text{He}$ interactions. The PESs for $\text{H}_2\text{O}$ interaction with $\text{He}$ and $\text{H}_2$ in general appear to pass the experimental DCS test with flying colors. Our results point out the differences between collisions of water with helium and with cold $\text{para-H}_2$, and suggest similarities in the shape of the DCS for all initial $\text{H}_2(J)$ states.

Various tests at lower collision energies, including $\text{H}_2–\text{H}_2\text{O}$ cluster spectroscopy, and scattering experiments testing the resonance or elastic regimes should be undertaken in parallel with more global tests such as pressure broadening or virial coefficient measurements. All these tests...
comparing theory with experiment help assess the validity of the H$_2$O–H$_2$ PES of paramount importance to understanding the abundance and role of water in the interstellar matter.

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