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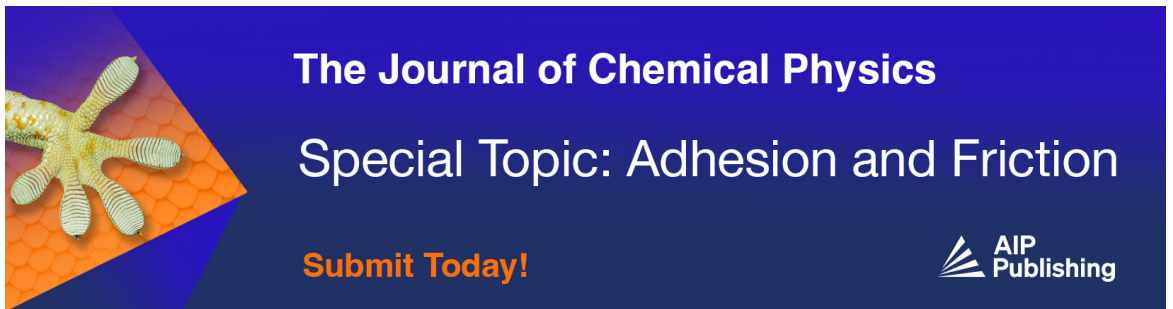


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# Molecular beam measurements of total collision cross sections of $\text{H}_2\text{O}^*$

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The total cross section for  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  scattering is measured with a supersonic nozzle beam system. The primary beam has a narrow velocity distribution, and the velocity is varied by control of the nozzle temperature. Velocities are determined by time-of-flight techniques. Cross sections obtained are averages over a Maxwellian distribution of the target molecules. Data at three velocities are presented. The cross sections for  $\text{H}_2\text{O}$  are surprisingly small, for example,  $3.07 \times 10^{-14}$  cm<sup>2</sup> at  $1 \times 10^5$  cm/sec, indicating little contribution from the dipole-dipole interaction.

## I. INTRODUCTION

Molecular beam scattering experiments have provided much useful information on atomic and molecular interactions. Intermolecular potentials can be extracted from measurements of differential scattering cross sections.<sup>1,2</sup> The most complete experiment of this type would involve crossed molecular beams of variable energy with velocity selection in each beam and a rotatable detector. In addition, if the angular dependence of the intermolecular potential is desired, state selection should be applied to both beams and to the detector. Due to the complexity and difficulty of such experiments, complete measurements of this type are rarely attempted. Fortunately, useful data can be extracted from much simpler experiments.<sup>1</sup> Even a total scattering cross section measurement can serve as a useful guide to theory, especially if done over a wide range of incident beam energy.

The  $\text{H}_2\text{O}$  molecule is of special interest as a candidate for scattering cross section measurements. The  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  intermolecular potential is poorly known, as is the interaction potential of water with other molecular and atomic species. Knowledge of these potentials is exceedingly important, for example, in studies of nucleation. The  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  scattering is also of particular interest since it represents a dipole-dipole collision. Some progress has been made recently in the understanding of the contribution of dipole-dipole interactions to intermolecular potentials and to scattering cross sections for linear dipoles and symmetric rotors.<sup>3,4</sup> However, the theoretical treatment has not yet been extended to asymmetric rotors. Experimental cross sections have usually been found to be large for scattering of molecules with appreciable dipole moments,<sup>4,5</sup> indicating large contributions from dipole-dipole interactions.

The only reported measurements on water to date are those of Kydd.<sup>6</sup> He used thermal beams (without velocity selection) to obtain total collision cross sections for  $\text{H}_2\text{O}$  on  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{H}_2\text{O}$ .

As part of a program of investigating the molecular interactions of  $\text{H}_2\text{O}$  in detail, we have, as a first step, studied the total scattering cross section for water. In

this experiment, the incident beam is produced by a supersonic nozzle source. Such a source offers the advantages of high intensity, wide range of beam velocities (through variation of nozzle temperature and seeding techniques), and narrow beam velocity distributions.<sup>7</sup> The scattering occurs in a static gas cell, hence the cross sections obtained are averages over the Maxwellian velocity distribution of the target gas. Measurements of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  total scattering cross section at three beam velocities are reported here.

## II. EXPERIMENT

The apparatus used in this investigation is shown schematically in Fig. 1. It is essentially conventional in design. The beam source, which can be used for many species of atoms and molecules, consists of a supersonic nozzle N (0.0075 cm diam) and skimmer SK (0.05 cm diam) of variable separation, with appropriate differential pumping. The nozzle can be operated over a wide range of temperatures and at pressures up to several atmospheres. (In the present experiment, the temperature of the nozzle was varied from 298 to 340°K, and the stagnation pressure was the vapor pressure of the water at each temperature used.) The beam can be produced with a pure gas or as a minority species in a lighter or heavier carrier gas, allowing a wide range of average beam velocities. Some variation of the beam velocity can also be achieved by variation of the nozzle temperature. In the work reported here, only the nozzle temperature is varied. Experiments with seeded beams are in progress.

After production and collimation in the source chamber, the beam enters a  $0.7 \times 0.7 \times 0.7$  m cubical chamber which is maintained at pressures below  $5 \times 10^{-7}$  torr, and which contains the scattering cell SC and the beam detector. The beam is chopped (usually at 100 Hz) at the entrance to the main chamber by a slotted wheel C driven by a synchronous motor. After passing through a narrow defining slit S and the scattering cell, the beam is detected by an electron bombardment ionizer I and quadrupole mass filter Q. The ion current from the Faraday cup F is measured with

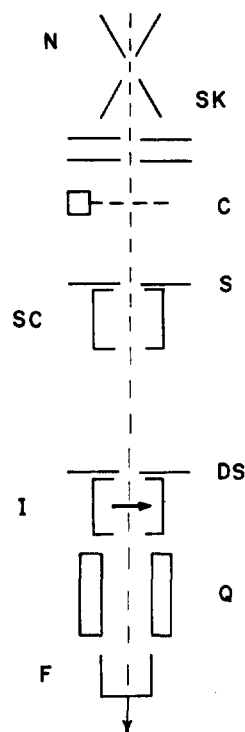


FIG. 1. Schematic diagram of apparatus for measurement of total scattering cross sections. Symbols are defined in the text.

a lock-in amplifier, synchronized to the chopping frequency.

The equivalent rectangular image of the beam at the detector slit DS is calculated to be of width 0.0095 cm. The scattering angle resolution is determined by the dimensions of S ( $0.0075 \times 0.65$  cm) and of DC ( $0.0075 \times 0.65$  cm), and by the distance from the center of SC to DC (16.66 cm). By the 50% criterion of Kusch,<sup>8</sup> the resolution is calculated to be  $8.3 \times 10^{-4}$  rad ( $171''$ ). The angular resolution is thus not particularly high, but should not lead to errors in measured cross sections of greater than 5% in most cases.

The scattering cell has a length of 2.44 cm, with beam channels of 1.32 cm length and  $0.029 \times 0.635$  cm cross section. Applying corrections for effusion of gas from the cell, the effective beam path length through the scattering gas is calculated to be 3.87 cm. (The calculation of the effective beam path length is similar to that of Rothe *et al.*<sup>9</sup>)

A prime consideration in the measurement of total scattering cross sections is the determination of the target gas density. In the present experiment, the pressure in SC is measured with an MKS Model 90 Baratron differential manometer. Pressures in SC are maintained constant or changed by a servo leak valve controlled by the output of the Baratron. For the present experiment, SC is maintained at 25°C, the Baratron head typically at 75°C. The pressure readings of the Baratron thus had to be corrected for thermal transpiration.

The use of Baratron differential manometers for pressure determination in scattering experiments has

been discussed by Utterback and Griffith<sup>10</sup> and by Bromberg.<sup>11</sup> According to Bromberg,<sup>11</sup> a Baratron is capable of an absolute accuracy of better than 0.5% with the factory dead weight calibration. The factory calibration is used in the present experiment. The instrument was compared with a new Model 77 Baratron, and no significant difference in calibration was noted. For the pressure range of the present experiment (less than  $7 \times 10^{-4}$  torr), random error of up to  $\pm 5\%$  in pressure measurement is possible due to resolution of the instrument.

High polymer concentrations can be produced by supersonic nozzle beams. In the present experiment, however, the product of stagnation pressure in the source and the nozzle diameter ( $P_0 d = 1.4$  torr·cm) is small enough that polymer concentrations should not be large with many gases.<sup>12</sup> By phase mass spectrometry Fricke, Jackson, and Fite<sup>13</sup> have found no evidence of a contribution from polymers to the mass 18 signal in a similar nozzle beam of water vapor. Consequently, we consider that the cross sections measured in the present experiment are appropriate to the pure H<sub>2</sub>O monomer.

A time-of-flight (TOF) technique is used for determination of beam velocities and velocity distributions. For this purpose, the chopper wheel is replaced by a wheel with a single narrow slot, and a multichannel analyzer with analog input is substituted for the lock-in amplifier. The light source reference at the chopper furnishes a pulse which is delayed by an appropriate amount before triggering the analyzer sweep. The timing circuits are calibrated with a precision time-mark generator. The signal is averaged over many cycles, then read out vs flight time on an XY recorder. (The TOF system is similar in many respects to that of Hagena and Varma.<sup>14</sup>)

The chopper motor in the present experiment is limited to relatively slow speeds. Consequently, the shutter function is of the same order of magnitude in time width as the distribution in flight times of the molecules in the beam. The detector signal  $S(t)$  may be written<sup>14</sup>

$$S(t) = \int_{-\infty}^{\infty} g(t') h(t-t') dt', \quad (1)$$

where  $g(t)$  is the shutter function and  $h(t) \propto t^{-1/2}(L/t)$ , the beam velocity distribution being  $f(v) = f(L/t)$ . The velocity distribution may thus be obtained by deconvolution of Eq. (1), using the measured detector signal as a function of time and the calculated shutter function. In the present experiment, the deconvolution is performed with the Fourier transform method and appropriate noise removal.<sup>15</sup> In all cases, the velocity distributions so extracted have a FWHM of less than 20%. The most probable velocity in the beam is in all cases greater than 80% of the asymptotic value<sup>16</sup>

$$u = (2C_p T_0 / m)^{1/2}$$

for supersonic nozzle beams. The accuracy of determination of the most probable beam velocities is better than  $\pm 5\%$  in the present work.

The usual procedure for cross section determination is followed in the present experiment.<sup>1</sup> At each beam velocity, the relative beam intensity  $I/I_0$  at the detector is measured as a function of target gas density  $n$ , and the effective cross section  $Q_{\text{eff}}(v_b)$  is calculated from the slope of a plot of  $\ln(I/I_0)$  vs  $n$ . The number so obtained must then be corrected for the velocity distribution of the target molecules. The incident beam velocity distribution is narrow enough so that no significant error is introduced by assuming that the beam is totally monoenergetic.<sup>17</sup> The appropriate correction is then the  $Fa_0(6, x)$  function of Berkling *et al.*,<sup>18</sup> assuming an inverse sixth power interaction potential. (No correction due to the density-sensitive detector is necessary with a monoenergetic beam.)

As a check on proper functioning of the apparatus, the argon-argon total cross section was measured. With due regard to the velocity dependence of the cross section, the value so obtained agreed within 3% with the results of Rothe and Neynaber.<sup>19</sup>

### III. RESULTS AND DISCUSSION

The total cross sections for H<sub>2</sub>O-H<sub>2</sub>O scattering as determined in this experiment are presented in Table I. Here  $v_b$  is the most probable beam velocity (measured as described above),  $Q_{\text{eff}}(v_b)$  is the effective cross section determined from plots of  $\ln(I/I_0)$  vs  $n$ , and  $Q(v_b) = Q_{\text{eff}}(v_b)/Fa_0(6, x)$  is the cross section at relative velocity  $v_b$ , assuming the target molecules to be at rest.<sup>18</sup> The potential constant is  $C^{(6)}$ , as derived from<sup>20</sup>

$$C^{(6)} = 5.676 \times 10^{-30} v_b Q^{5/2}(v_b) \text{ erg} \cdot \text{cm}^6,$$

assuming an inverse sixth power interaction potential energy.

The values of  $Q_{\text{eff}}(v_b)$  are reproducible to within  $\pm 5\%$ . Most of the scatter in the value of the cross section determined at a particular beam velocity can be attributed to random error in pressure measurement. Considering possible sources of systematic error, including resolution, we estimate the 90% confidence limits of the total probable error to be  $\pm 10\%$  in the results for  $Q_{\text{eff}}(v_b)$  and  $Q(v_b)$  presented in Table I. The probable error for the derived values of  $C^{(6)}$  include the probable error in the measurement of the beam velocity, as well as that in measurement of the cross section.

Kydd<sup>6</sup> has measured the H<sub>2</sub>O-H<sub>2</sub>O cross section using crossed effusive beams at beam source temperatures of 252–518°K. At 338°K, corresponding to  $v_b = 5.6 \times 10^4$  cm/sec, he found an average cross section  $Q(v_b)$  of  $615 \pm 65 \text{ \AA}^2$ , leading to a potential constant of  $610 \pm 150 \times 10^{-60} \text{ erg} \cdot \text{cm}^6$ . Correcting to the value appro-

TABLE I. Experimental H<sub>2</sub>O-H<sub>2</sub>O total cross sections and potential constants as a function of beam velocity.

$Q_{\text{eff}}(v_b)$ ( $\text{\AA}^2$ )	$v_b$ ( $10^4$ cm/sec)	$Q(v_b)$ ( $\text{\AA}^2$ )	$C^{(6)}$ ( $10^{-60}$ erg·cm <sup>6</sup> )
346	9.2	320	96±35
333	9.6	310	92±35
328	10.0	307	94±35

prate to a beam velocity of  $1.0 \times 10^5$  cm/sec (assuming that  $Q \propto v^{-0.4}$ ), we obtain  $482 \text{ \AA}^2$  for Kydd's cross section, yielding a discrepancy of about 50% with our results (and a factor-of-6 discrepancy in the potential constant). That Kydd used the Rosen and Rabi procedure<sup>21</sup> rather than the procedure of Berkling *et al.*<sup>18</sup> for data reduction is not sufficient to explain the discrepancy. The angular resolutions in the two experiments are probably not significantly different, although it is difficult to estimate the resolution in Kydd's experiment. An adjustable defining slit was used, and results were extrapolated to zero width. However, at defining slitwidths nominally leading to resolution comparable to that of the present experiment, the detector slitwidth was larger than the effective width of the beam at the detector. Thus, a loss in detection of small-angle scattering would have occurred. Insufficient resolution would not, however, explain the discrepancy with the present results, since the true cross section would then have been even higher in Kydd's experiment.

Wendell, in unpublished work,<sup>22</sup> has found  $Q(v_b) = 330 \pm 50 \text{ \AA}^2$  at  $v_b = 5.15 \times 10^4$  cm/sec. Although this value (when corrected for velocity) is lower than the present results, it represents fair agreement with the present experiment, since Wendell's angular resolution was low. In view of these results, we are inclined to believe that a systematic error was present in Kydd's experiment.

Kydd<sup>6</sup> has calculated a theoretical value of  $313 \times 10^{-60} \text{ erg} \cdot \text{cm}^6$  for  $C^{(6)}$ , in which the dipole-dipole contribution (assuming the Keesom<sup>23,24</sup> relation) is  $173 \times 10^{-60} \text{ erg} \cdot \text{cm}^6$ , and the dispersion contribution (from the Slater-Kirkwood formula<sup>25,26</sup>) is  $130 \times 10^{-60} \text{ erg} \cdot \text{cm}^6$ . Our values for  $C^{(6)}$  are thus much lower than simple theory would predict, unless the dipole-dipole interaction is essentially absent.<sup>27</sup> However, application of the Keesom relation,

$$C_{d-d}^{(6)} = 2\mu_1^2\mu_2^2/3kT_{\text{eff}},$$

to the H<sub>2</sub>O-H<sub>2</sub>O interaction is questionable. The Keesom potential is related to (but not necessarily an accurate description of) second-order dipole-dipole interactions, which are only appreciable when one of the colliding molecules is in the  $J=0$  state.<sup>3</sup> First-order dipole-dipole effects<sup>3,4</sup> (which are inelastic) may be small in the H<sub>2</sub>O case because of the large rotational state spacings. Unfortunately, a detailed treatment of the dipole-dipole interaction for H<sub>2</sub>O is not possible at

the present time, since the theory has not yet been extended to asymmetric rotors.

It should be noted that a nozzle beam source extracts internal energy from the beam molecules during the expansion.<sup>7</sup> Consequently, the rotational state populations of the beam molecules are appropriate to a low temperature. If the dipole-dipole interaction were appreciable, a different cross section might be measured with a nozzle source than with an effusive source. That such an effect is not large in the case of H<sub>2</sub>O may be inferred from the apparent agreement of the present results with those of Wendell<sup>22</sup> (who used effusive beams).

#### IV. CONCLUSIONS

The results of the present study indicate that under particular experimental conditions (supersonic nozzle beam incident upon a static gas), and over a limited velocity range, the contribution of the dipole-dipole interaction to the H<sub>2</sub>O-H<sub>2</sub>O total scattering cross section is small. The data are consistent with an inverse sixth power interaction potential since no significant variation of the potential constant with velocity was observed. Such a variation would be expected if significant contributions from either first- or second-order dipole-dipole interactions are present. It is apparent that the true form of the velocity variation of the H<sub>2</sub>O cross section, and consequently the role of the dipole-dipole interactions, can only be clarified by measurements of the cross section over a wide velocity range.

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