Gas transport across an air/water interface populated with capillary waves

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An experimental study of gas transport across an air/water interface, populated by a field of standing capillary waves is presented. The experiments were conducted in a small tank containing distilled water, enriched with carbon dioxide. The capillary waves were of the Faraday type, generated by providing a small vertical vibration to the water tank. The frequency of excitation was varied from 200 to 400 Hz, giving wavelengths from 3.62 to 2.26 mm (linear estimate). The gas transport rate across the interface increased by almost two orders of magnitude as the wave slope was increased from zero to slightly above 0.2 m/m. A unique aspect of these experiments is that capillary waves were isolated from the obfuscating effects of turbulence, aerosol generation, and other phenomena typically present in wind/wave tunnel experiments. Consequently the large enhancement in gas transfer was due to the effects of capillary waves alone, demonstrating their importance in gas exchange processes. The maximum mass transfer coefficients obtained in these experiments are not achieved in typical wind/wave tunnel experiments below wind speeds of 10 m/s. © *1997 American Institute of Physics.* [S1070-6631(97)02408-2]

I. INTRODUCTION

The oceans which cover the surface of the earth have an enormous capacity to absorb heat and dissolved gases. Accordingly, the rate at which heat and mass are transferred across the air/sea interface greatly affects the weather as well as the long term status of the environment. The development of climatological models requires an understanding of the various parameters and phenomena which mediate the transfer of heat and mass across this interface. Waves have been shown to enhance transport across the air/water interface. However, in spite of significant experimental and analytical efforts, an understanding of how and to what degree waves affect transport remains elusive. The objective of the experiments described herein is to develop an understanding of the role that capillary waves play in the transport of dissolved gases across the air/water interface. CO2 was chosen for these experiments because of the ease with which its concentration can be measured, and also because of its importance as a greenhouse gas. It should be noted that the results are also applicable to other dissolved gases and, to a certain extent, to the transfer of heat.

A large part of the experimental work dedicated to understanding air/sea transport has been performed in wind/ wave tunnel facilities where transport processes in open sea environments are simulated by wind generated waves in a long water tunnel. Figure 1 presents an example of the results of such a study, where data due to Ocampo-Torres *et al.*¹ is presented. This figure is a plot of the mass transfer coefficient for carbon dioxide, *K*, versus the wind speed *u*. The data show that *K* is small and only weakly dependent on *u* when *u* is small, and that *K* is much larger and more sensitive to *u* at higher wind speeds. A clear break in the data, separating these two regimes, occurs at a critical wind speed, which for this study occurs at $u \cong 3$ m/s. The authors noted that this critical wind speed corresponds to the lowest value of u at which waves are observed. This observation is found throughout the literature on this topic. Moreover, it is almost always true that the waves which are observed at this critical wind speed are capillary waves. For example, Kanwisher² observed a sudden increase in the rate of CO₂ outgassing in a wind/wave tunnel, at a wind velocity of about 3 m/s, and found that this sudden increase occurred at approximately the same wind speed for which capillary waves first formed. Broecker et al.³ found similar behavior for CO₂ outgassing from water in a slightly deeper wind/ wave tunnel, where the sudden increase in K occurred at slightly above 2 m/s, which also coincided with the formation of capillary waves. Downing and Truesdale⁴ performed experiments on the transport of O₂ into water, in a wind/ wave tunnel, and found a sudden increase in the transport rate at a critical wind velocity of 3 m/s. They report that this sudden increase in K coincided with the appearance of wavelets and ripples. Discontinuities in K versus u data were also observed by Hoover and Berkshire⁵ for CO₂ and by Liss⁶ for both CO₂ and O₂, however, no discussion of the wave field was provided.

Jähne *et al.*⁷ did experiments in a circular wind/wave tunnel for both CO_2 and N_2 . In these experiments, a sudden increase in the gas transport rate was observed when the water surface went from "smooth" to "rough." Although information concerning the size of the waves which roughened the surface was not provided, experiments conducted in the same facility, using ethanol/water solutions, showed a break in the data and a roughening of the surface at a much lower wind speed. Since ethanol/water mixtures have a lower surface tension than pure water, there is reason to believe that the sudden roughening of the surface and concomitant increase in mass transfer coefficient at the lower wind speeds were due to surface tension dominated waves, i.e., capillary waves.

The aforementioned experiments suggest that capillary waves play an important role in gas transport, however, sev-

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FIG. 1. Typical plot of mass transfer coefficient *K* versus wind speed *u* in a wind/wave tunnel. Data due to Ocampo-Torres *et al.*¹ for CO_2 transport.

eral questions have not yet been addressed. First, while it is true that a sudden increase in transport occurs at the same wind speed for which capillary waves are first observed, a causal relationship has not been demonstrated, and the possibility that the two observations occur coincidentally has not been ruled out. Second, even if it is true that capillary waves contribute to the sudden increase in mass transfer at the critical wind speed, many other factors also contribute to transport, and the relative contribution due to capillary waves is unknown. It is not clear, for example, what fraction of the transport is due to air and water turbulence, bubble entrainment, etc. Finally, if capillary waves are in fact responsible for a significant amount of mass transport, the physical mechanism of their contribution needs to be identified. For example, it has been suggested that these waves may act to trip the air flow from a laminar to a turbulent state,⁴ and a similar conjecture for the water side could also be made. It is also possible that it is the inherent hydrodynamics of the capillary waves themselves which cause the enhanced transport by, for example, rectified diffusion, as has been analytically investigated by Szeri⁸ for Crapper⁹ waves. Also, the increase in surface area caused by capillary waves must also contribute to the transport. In any event, determining the actual mechanism by which capillary waves contribute to gas transport is an outstanding issue.

None of the aforementioned questions can be adequately addressed by wind/wave tunnel experiments alone; so many factors which affect transport exist in parallel that the role which capillary waves play cannot be ascertained. Some work has been done to isolate capillary waves and ascertain their contribution to gas transport. For example, Witting¹⁰ performed an analysis of capillary waves for the case of heat transfer and found an enhancement of transport by as much as a factor of 9.0 for Crapper waves of limiting amplitude. MacIntyre¹¹ has analyzed Crapper waves and demonstrated that they enhance gas transport by as much as a factor of 3.5 over that of a flat free surface. MacIntyre also presented experiments for CO₂ transport through a water surface,

populated by capillary waves, in which the water was simultaneously stirred in the bulk via a magnetic stirrer. The capillary waves were created by exciting a flask with an acoustic speaker at a frequency of 100 Hz, giving a wavelength of \sim 3 mm and a wave amplitude of \sim 0.2 mm. The data reveal that capillary waves with stirring enhance CO₂ transport by, at most, 30% over stirring alone. The meaning of these results is somewhat obscured by the lack of information concerning the stirring. If the turbulence generated below the surface was very strong, even a significant increase in transport due to the capillary waves would be seen as a relatively small increase with respect to the turbulent transport. Surprisingly, the data of MacIntyre¹¹ indicate that, for constant wave parameters, an increase in the stirring rate results in an increase in the relative contribution due to the capillary waves. An explanation for this result is not presented. In any event, experiments which go beyond the preliminary work of MacIntyre¹¹ are needed. Specifically, experiments where there is no externally imposed turbulence or bulk liquid flow are needed so that the contribution of capillary waves can be isolated.

The proposed experiment is an idealized case that does not account for the nonlinear interactions which occur between waves and turbulence, among other things. Moreover, as noted by Jähne *et al.*,¹² since capillary waves obtain energy from larger scale gravity waves, it is also important to study gravity waves. Nevertheless, a large number of wind/ wave tunnel studies, along with existing analytical work all seem to suggest that capillary waves play an important role in air/sea gas exchange. Consequently, experiments which isolate capillary waves and accurately ascertain their contribution to gas transport in a controlled environment are an important first step toward understanding their role in the actual air/sea environment.

In the work described herein, we isolate capillary waves by generating them independently of any air or water motion. A small tank of water is subjected to very small vertical vibrations to create capillary waves via the Faraday instability. There is no wind or bulk stirring of the liquid. Hence any enhancement of gas transport, above that of pure diffusion and background natural convection, is due solely to the inherent hydrodynamics of capillary waves.

II. EXPERIMENTAL METHOD

The capillary waves which were investigated in this work were Faraday waves,¹³ generated by vibrating a small tank in the vertical direction. When excited in this fashion the water surface experiences a parametric instability and waves are generated at one half the driving frequency. The theory describing these waves has been investigated by several authors^{14–20} and a review can be found in Miles and Henderson.²¹ Gollub and co-workers^{22,23} and Meron and co-workers^{24,25} have used Faraday waves as a platform for studying chaotic dynamics in spatially extended systems. The motion of particles and dye interfaces on the surface of Faraday waves has also been investigated. Ramshankar *et al.*²⁶ used fractional Brownian motion to describe the transport of particles on the surface, and Ramshankar and Gollub²⁷ used fractal dimensions to characterize the isocon-

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FIG. 2. Schematic illustration of experimental setup. For details of the optics used between the laser exit and the PSD sensor, see Fig. 6.

centration contours of dye interfaces on the surface of Faraday waves. Other than the preliminary work of MacIntyre,¹¹ however, Faraday waves have not been used as a platform for studying the effects of capillary waves on gas exchange processes.

The experimental apparatus used in the experiments is illustrated in Fig. 2. Waves were generated in a small plexiglass tank whose interior dimensions were 5 by 5 by 1.75 in. deep. The tank was mounted on an electrodynamical shaker (Vibration Test Systems, VTS65) which was powered by a Techron 5515 power supply amplifier. A sine wave was fed to the amplifier from a function generator (HP 3325A) which was used to control the amplitude and frequency of the tank excitation. A pH meter having an accuracy of ± 0.005 pH units (Orion, model 290A) was used to monitor the pH of the tank water. A temperature compensated pH electrode was located below the water surface, and the pH values were used to measure the CO₂ concentration, as described in the following section. Data from the pH meter was continuously sent to a computer which controlled data acquisition. Two accelerometers (Endevco, model 2221D) were mounted on the water tank. One accelerometer was oriented in a direction parallel to the shaker motion, and the other in a direction perpendicular to the shaker motion. These accelerometers monitored the motion of the tank in the on-axis (direction of shaker motion) and off-axis direction (direction perpendicular to shaker motion). The signals from these two accelerometers were sent to Unholtz Dickie charge amplifiers (model D22) whose output was monitored on an oscilloscope, sent to an A/D converter, and stored on the computer. A photograph of a typical Faraday wave field obtained from this apparatus is presented in Fig. 3.

The primary results of the experiments described here were plots of mass transfer coefficient K versus wave slope S, for several excitation frequencies f. The means by which

these two quantities were measured will now be described.

A. Wave slope measurement

Several optical methods exist for the measurement of wave slope. We chose to use the relatively simple method described in Sturm and Sorrell,²⁸ wherein a laser beam is vertically directed from beneath the water surface and a measurement of the beam displacement, caused by refraction of the angled air/water interface, is used to obtain the wave slope. In wind/wave tunnel experiments, waves having amplitudes greater than 1 cm are common, and an error in the measurement is introduced by the variation in the distance between the water surface and the optical detector used to measure the refracted beam displacement. More sophisticated laser based wave slope measurement techniques have been developed to eliminate this error.²⁹⁻³⁴ Techniques which permit the instantaneous measurement of wave slope over a two-dimensional region have also been developed.^{35,36} Although a method for measuring the wave height was not utilized for the experiments presented herein, observation of the wave surface, while holding a scale near the tank edge, showed that the wave height was always less than 1 mm. Consequently, the distance between the water surface and the detector varied very little, obviating the need for a more advanced measurement technique. The maximum error introduced by the variation in the distance between the water surface and the detector due to the maximum possible peakto-trough wave height of 1 mm was 2%.

A schematic illustration of the wave slope measurement method is presented in Fig. 4. A two-dimensional position sensitive detector (On-Trak, OT300 amplifier with 2L20SP detector) was located a distance L above the water surface. The two voltage outputs from the position sensitive detector (PSD), V_x and V_y , were linearly related to the x and y loca-



FIG. 3. Photograph of the water tank, excited at a frequency of f = 88 Hz. The tank water is dyed for visualization purposes in this photograph, and a sheet of white paper has been placed beneath the normally transparent tank floor.

tion of the laser spot striking the detector surface via the relations

$$x = V_x / C_x \tag{1}$$

and

)

$$v = V_y / C_y, \qquad (2)$$

where C_x and C_y are the calibration constants relating the output voltage to the laser spot displacement in the two coordinate directions. The PSD was mounted on a precision three-dimensional stage (L. S. Starrett Co.) having a positioning accuracy of 2.5 μ m, which was adjusted so that V_x and V_y were zero when the water surface was flat. Thus after obtaining C_x and C_y the total displacement, d, of the laser beam was obtained from the relation

$$d = \sqrt{(V_x/C_y)^2 + (V_y/C_y)^2}.$$
 (3)

Using Snell's law and the geometry shown in Fig. 4, the wave slope at the location where the laser pierces the water surface is given by the relation

$$S = \frac{d/L}{1 - (n_w/n_a)\sqrt{1 + (d/L)^2}},$$
(4)

where n_w and n_a are the indices of refraction for water and air, respectively.

Calibration of the PSD to obtain C_x and C_y was performed by translating the precision stage and recording position and voltage. A least-squares fit to the data was then performed to get C_x and C_y . The PSD was mounted so that the x and y axes of the PSD were parallel to the x and y axes of motion for the translation stage. The voltage-displacement characteristics of the PSD were very linear and highly reproducible. A sample calibration is presented in Fig. 5. The calibration was repeated periodically, and the maximum variation in the calibration constant was found to be less than 1% over a two month period. The average calibration constants were $C_x = 958.45$ V/m and $C_y = 956.44$ V/m. V_x and V_y were continuously sampled throughout the experiment so that the slope S was continuously recorded.

Errors due to background room lighting and stray light sources were virtually eliminated by mounting a laser line bandpass interference filter in front of the PSD detector. The center wavelength of the filter is tuned to the helium neon laser line, $\lambda_c = 632.8$ nm and has a bandwidth of 12 nm, effectively filtering out all light except that corresponding to the laser beam.

An optical method was devised to provide an accurate measurement of L which, according to Eq. (4), is necessary to obtain the wave slope. A prism of known diopter value (centimeters of beam deflection at 1 m from the prism) was placed on the dry tank floor. The distance that the beam is deflected by the prism is measured by the calibrated PSD. By locating the prism so that the laser beam passed through it at a location where its height had been measured using a micrometer, the distance from the tank floor to the detector was calculated using the diopter value of the prism (17.60 diopters). This distance was then used to compute the distance from the water surface to the detector, using the known water height. For all of the experiments presented herein, the water height was 1.860 cm and the water surface to detector distance was 4.602 cm.

The laser beam used for the laser slope gauge (Uniphase,



FIG. 4. Geometry of the refraction of a laser beam as it pierces the water surface.

HeNe, 0.8 mW) had a beam diameter of 0.48 mm $(1/e^2)$ value), and so it was necessary to focus the beam to achieve adequate spatial resolution of the wave slope. The optical apparatus used to focus the beam down to a small measurement volume is illustrated in Fig. 6. The beam is first expanded by a factor of 10 using the two lens assembly, L1 and L2. Lenses L1 and L2 have focal lengths of 10 and 100 mm, respectively, and are separated by a distance equal to the sum of their focal lengths. This results in a collimated beam having a $1/e^2$ diameter of 4.8 mm. This expanded beam is passed through an iris to remove any irregularities at the peripheral regions of the beam and is focused by lens L3 (f = 500 mm) down to a small measurement volume. A right angle prism was located between lens L3 and the measurement volume to redirect the beam into the vertical direction. The location of lens L3 was adjusted so that the focal point was located at the water surface. Exactly the same quantity of water was used for all experiments, so the location of the focal point did not have to be changed from run to run. Each optical element was adjusted to ensure that the laser beam was centered and normal to the lens. Additionally, the orientation of the shaker was adjusted so that the tank floor and the water surface were normal to the laser beam, insuring that the beam direction coincided with the gravity vector.

The diameter of the beam at the focal point was measured by mounting a razor blade onto a precision translation stage (positional accuracy of 2.5 μ m). The razor blade was located just above the water surface, and the stage was then translated in the horizontal direction. The position at which



FIG. 5. Sample calibration of the PSD detector. The output voltages V_x and V_y are plotted as a function of the displacement of the PSD in the x and y directions, respectively. This particular calibration yielded calibration constants of C_x =960.281 V/m and C_y =958.487 V/m.

the blade just perturbed the image of the beam on a white screen located well above the tank, and the position at which the beam image was completely extinguished by the blade, were recorded, and the difference was taken as the spot diameter. A value of 250 μ m was obtained using this method, which yields a beam diameter considerably larger than the $1/e^2$ diameter typically cited. The $1/e^2$ diameter computed using diffraction limited optics for a Gaussian beam³⁷ was 84 μ m. The actual $1/e^2$ diameter lies somewhere between these two values. As demonstrated by Cox,³⁶ satisfactory resolution of the wave slope can be obtained when the radius r_0 of the light spot is less than $\lambda/6.8$. The minimum water wavelength for the experiments presented here is $\lambda = 2.26$ mm, requiring $r_0 < 330 \ \mu$ m. Thus even our overestimate of the beam diameter, which gives $r_0 = 125 \ \mu m$, is sufficient to resolve wave slope for the parameter space explored here. The depth of focus at the focal point (length over which the beam diameter varies by less than 5%) was computed to be 5.6 mm. The peak-to-trough wave height was less than 1 mm for all experiments indicating that the water surface was always situated at the focal point of the laser beam.



FIG. 6. Optical apparatus for laser beam focusing.

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B. Measurement of mass transfer coefficient

The change in the CO_2 concentration due to transport across the air/water interface is described by the equation

$$\frac{\partial C_w}{\partial t} = \frac{-K}{h} \left(C_w - \frac{C_a}{H} \right),\tag{5}$$

where C_w is the concentration of CO₂ in the water, C_a is the concentration of CO₂ in the air, *h* is the height of the water, and *H* is the Henry's law constant which accounts for the degree of solubility of CO₂ in the water. Integrating Eq. (5) over time gives

$$C_w = \left(C_{w,0} - \frac{C_a}{H}\right) e^{-K/ht} + \frac{C_a}{H},\tag{6}$$

where *t* is time and $C_{w,0}$ is the concentration at t=0. Assuming the hydrodynamics do not change during the course of an experiment, Eq. (6) requires that the C_w versus *t* data yield a straight line of slope -K/h, when plotted on semilogarithmic coordinates. Values for *K* were obtained by performing a least-squares fit to the time traces of $\log[CO_2]$. For these experiments the $\log[CO_2]$ time traces were relatively straight (see Sec. III). Nevertheless, *K* was computed by first breaking the time traces up into smaller segments and then computing *K* from each subset of the time trace so that small fluctuations in the hydrodynamics of the system did not produce erroneous values for *K*.

The CO₂ concentration was obtained from the pH data using the relationship which exists between $[CO_2]$ and pH for pure water. Following Stumm and Morgan,³⁸ the dissolution of CO₂ in water results in the equilibration of the species $[H^+]$, $[OH^-]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H_2CO_3]$, and $[HCO_3^-]$, governed by the chemical equilibrium equation

$$[CO_{2}]+[H_{2}O] \rightleftharpoons [H_{2}CO_{3}] \rightleftharpoons [H^{+}]+[HCO_{3}^{-}] \rightleftharpoons 2[H^{+}]$$
$$+[CO_{3}^{2^{-}}], \qquad (7)$$

where [-] denotes concentration in moles/m³. Equation (7) can be written as a set of five algebraic equations relating the concentrations of all species present.

$$2[CO_3^{2-}] + [HCO_3^{-}] + [OH^{-}] = [H^{+}],$$
(8)

$$k_1 = \frac{[\mathrm{CO}_2]}{[\mathrm{H}_2\mathrm{CO}_3]},\tag{9}$$

$$k_{\rm H_2CO_3} = \frac{[\rm HCO_3^-][\rm H^+]}{[\rm H_2CO_3]},$$
(10)

$$k_2 = \frac{[\mathrm{CO}_3^{2^-}][\mathrm{H}^+]}{[\mathrm{HCO}_3^{-}]},\tag{11}$$

$$k_w = [H^+][OH^-].$$
 (12)

Equation (8) imposes charge neutrality on the system, and Eqs. (9)–(12) impose chemical equilibrium for the species concentration via the constants k_1 , k_2 , $k_{H_2CO_3}$, and k_w . Combining these equations into a single relation for [CO₂] yields

$$[CO_2] = \frac{k_1}{k_{H_2CO_3}} \frac{[H^+]([H^+]^2 - k_w)}{(2k_2 + [H^+])}.$$
 (13)

The values for the equilibrium constants are k_1 =650, $k_{\text{H}_2\text{CO}_3}$ =2.897×10⁻⁴, k_2 =4.69×10⁻¹¹, and k_w =1×10⁻¹⁴, all obtained at 25 °C.³⁸

Converting pH to $[H^+]$ using the definition for pH,

$$pH = -\log[H^+], \tag{14}$$

and then substituting $[H^+]$ into Eq. (13) provides the $[CO_2]$ time traces necessary to compute *K* from Eq. (6).

Sample plots of wave slope time traces are presented in Figs. 7(a)-7(d). As noted earlier, Faraday waves oscillate at a frequency f_w , which is one-half that of the excitation frequency f. Hence in these figures, the dominant frequency will be observed at one-half the indicated excitation frequency, f. In Fig. 7(a), the first two seconds of a run at an excitation frequency of 200 Hz is presented. A time trace of the same duration at an excitation frequency of 400 Hz is presented in Fig. 7(b). A close up of the first 0.1 s of the time traces are presented as well. The behavior observed in Fig. 7 is mirrored in the physical appearance of the water surface during the course of the experiment. An ordered collection of nodes and antinodes is observed over the entire surface. The up and down motion of the waves is too fast for the eye to observe, but is seen as the rapidly changing wave slope which is apparent in Figs. 7(c) and 7(d). The entire wave pattern is observed to slowly translate about the tank, and this translation is manifested as the low-frequency modulation of the wave slope, as seen in the time traces of Figs. 7(a)and 7(b). This modulation occurs more rapidly as the amplitude of shaking is increased, and as the frequency of excitation is increased. This modulation also permitted an accurate sampling of the wave slope using our technique where the laser, and therefore the measurement location, is fixed in space. Because the wave field drifted randomly over the measurement location, all phases of the wave were measured. This modulation is due to a random drift current and is probably responsible for some degree of mixing, as will be discussed in Sec. III.

C. Experimental procedure

Prior to starting the experiments, the pH meter was calibrated using calibration buffers (Sigma Chemical). Care was taken to thoroughly wash the pH probe with triply distilled water after calibration, since contamination of the tank water with the buffer would have invalidated the relationship between pH and [CO₂]. In a separate flask CO₂ was bubbled through triply distilled water for about 30 min. When the pH in the flask reached ~4.0, 300 ml of the water was transferred into the wave tank. The glassware used in this transfer process, as well as all objects used near the wave tank, were cleaned with methanol and then rinsed with triply distilled water and blown dry prior to each use in order to prevent contamination of the wave tank. Powderless latex gloves were worn at all times when handling the glassware or working near the tank.

After filling the tank, the location of the PSD detector in the plane above the water surface was adjusted to zero out V_x and V_y . The most recent PSD calibration was loaded into the program which controlled the data acquisition system,

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FIG. 7. Time traces of wave slope for two runs. Two seconds of data are presented in (a) and (b) and a close up of the first 0.1 s of data are presented in (c) and (d).

and the shaker was powered up and set at the desired amplitude and frequency. The system was run for 5 min to reach a steady state, and then data taking was initiated.

During the course of the experiments, the output from the pH meter, the PSD outputs, and the on-axis and off-axis accelerometer outputs were continuously sampled. At the completion of the experiment, the pH time traces were converted into $[CO_2]$ time traces using the relations described in the previous section. The mass transfer coefficients *K* were extracted from this data, and the PSD outputs were converted to wave slope *S*. An experiment typically lasted 20 to 30 min.

As mentioned above, extreme care was taken to maintain the cleanliness of the system. The primary reason for this was to eliminate the introduction of anything that might contaminate the water used in the system and thereby invalidate the relationship between pH and $[CO_2]$. We had also hoped to eliminate the presence of surfactants. However, in spite of our precautions, it is most likely the case that a surfactant monolayer always existed on the water surface. It should be noted that the same experimental procedure was strictly followed from experiment to experiment so that any surfactants which were introduced might at least be introduced in a repeatable fashion. No measurements of elasticity or surface tension were made.

Experiments were run at excitation frequencies of f= 200, 240, 280, and 400 Hz, resulting in wave frequencies $f_w = 100, 120, 140, and 200$ Hz, respectively. A summary of the values of f, f_w , and the resulting wavelength λ used during these experiments is presented in Table I. Note that λ is obtained from the linear dispersion relationship,³⁹

$$c^{2} = \left\{ \left(\frac{g\lambda}{2\pi}\right) \left[\frac{(\rho - \rho')}{\rho}\right] + \left[\frac{\sigma}{(\rho + \rho')}\right] \left(\frac{2\pi}{\lambda}\right) \right\} \tanh\left(\frac{2\pi}{\lambda}\right) h,$$
(15)

where c is the phase speed of the wave, σ is the surface tension, g the gravitational acceleration, λ the wavelength, ρ the water density, ρ' the air density, and h the water height. The value of λ is obtained by substituting $c = \lambda f_w$ in the left-hand side and then solving for λ . The value used for surface tension was 7.18×10^{-2} N/m.

TABLE I. Values of the wave frequency f_w and λ corresponding to each value of the excitation frequency f used in the experiments. Values for λ are obtained from the linear dispersion relationship.

f (Hz)	f_w (Hz)	λ (mm)
200	100	3.62
240	120	3.19
280	140	2.87
400	200	2.26

The ratio of the on-axis acceleration to the off-axis acceleration, as quoted by the shaker manufacturer is 5%. We measured this ratio (rms on-axis acceleration to rms off-axis acceleration) to be 6%, 5.7%, 25%, and 21% at f = 200, 240, 280, and 400 Hz, respectively. While large off-axis tank accelerations can result in "sloshing" modes, no such modes were observed in our experiments. Off-axis accelerations can also induce secondary flows and bulk mixing beneath the wave surface. The existence and effects of such bulk mixing are discussed in Sec. IV.

For the largest wavelength, the ratio of the tank length to the wavelength was 35, eliminating the effect of the walls on the essential wave dynamics. The slopes varied from zero to an average wave slope just above 0.2 m/m.

III. RESULTS

As described in the previous section, the mass transfer coefficient *K* is directly obtained from the slope of the $[CO_2]$ time traces plotted on semilogarithmic coordinates. Figure 8 is a plot of log $[CO_2]$ versus time for 35 sample runs, obtained at an excitation frequency of f = 400 Hz. The time traces were obtained at several different excitation amplitudes. The data from each run are reasonably well-fit by a straight line. However, small variations in the local slope of each time trace are present. To reduce the effect of this small variation on the data, each time trace was broken into several



FIG. 8. Plot of $\log[CO_2]$ versus time for sample runs at an excitation frequency of f = 400 Hz. The $[CO_2]$ concentration is normalized to its value at t = 0.



FIG. 9. Plot of mass transfer coefficient K versus average wave slope S, for all four excitation frequencies. A parabolic curve fit is included for each data set. The error bars were obtained from the entire data set at each excitation frequency.

subsegments which were then used to obtain separate values of *K*. The resulting data were then averaged in wave slope bins having a width of 0.01 m/m. A plot of the resulting data is presented in Fig. 9, where *K* is plotted against the average wave slope \overline{S} , for each of the four excitation frequencies. A parabolic curve fit of the form

$$K = B_1 + B_2 \overline{S}^2 \tag{16}$$

is provided for each data set. The values of B_1 and B_2 for each excitation frequency f are presented in Table II. The length of the error bars in Fig. 9 is equal to two standard deviations of the data set for that frequency.

Jähne¹² states that the mass transfer coefficient is most appropriately correlated to the mean-square wave slope. It is unclear, however, whether the mean-square slope has the average wave slope subtracted or not. Consequently, we have considered two different definitions of this quantity, defined in Eqs. (17) and (18) as S' and S'', respectively,

$$S' = (S - \overline{S})^2, \tag{17}$$

$$S'' = \overline{S^2}.$$
 (18)

Figure 10 is a plot of K against S', and Fig. 11 is a plot of K against S''. Note that they are qualitatively identical and that the data are well fit by a straight line in both cases.

TABLE II. Values of the coefficients B_1 and B_2 used in the parabolic curve fit [Eq. (16)] in Fig. 9.

f (Hz)	<i>B</i> ₁	<i>B</i> ₂
200 240 280 400	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.0349 0.077 0.116 0.178

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FIG. 10. Plot of *K* versus mean-square wave slope defined as $S' = (\overline{S - \overline{S}})^2$ for all four excitation frequencies. A linear curve fit is included for each data set.

In some of the higher amplitude runs (none of which were included in Figs. 9-11) the waves were steep enough that the refracted laser beam was deflected off the detector. The data collection system registered these events by recording a warning message in a log file. Since the wave slope measurements obtained while the laser beam is off the detector are wrong, the average slope obtained during these runs is invalid and was not used. The measurements of K for these runs, however, were valid. In an attempt to utilize this data, the wave slope for these "off-detector" runs was extrapolated from the accelerometer data. Figure 12 is a plot of \overline{S} as a function of the on-axis accelerometer output for all of the runs where the wave slope did not leave the PSD detector. These data are reasonably well fit by a straight line, and so the accelerometer output from runs where the wave slope was too large to be recorded by the detector was determined



FIG. 12. Plot of \overline{S} versus on-axis mean-square accelerometer output at f = 240 Hz.

by using this linear fit to extrapolate the actual wave slope. This method is crude; nevertheless, it permits the use of data that would otherwise be discarded. The results are plotted in Fig. 13. Note that in this figure the data of Fig. 9 are being supplemented with the extrapolated, higher wave slope data. A parabolic curve fit of the form given in Eq. (16) is included in Fig. 13. The constants B_1 and B_2 are presented in Table III. Note that the scatter in Fig. 13 is significantly larger than in Fig. 9, which is not surprising since extrapolating the wave slope from the accelerometer output is much less accurate than a direct wave slope measurement. Our reason for presenting this data is simply to illustrate the very large mass transfer coefficients which were obtained from these moderate slope waves, even though the exact values for wave slope at the high end of Fig. 13 are questionable. We



FIG. 11. Plot of K versus mean-square wave slope defined as $S'' = \overline{S^2}$ for all four excitation frequencies. A linear curve fit is included for each data set.



FIG. 13. Plot of K versus \overline{S} , where the large values of \overline{S} are extrapolated from the accelerometer output.

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TABLE III. Values of the coefficients B_1 and B_2 used in the parabolic curve fit [Eq. (16)] in Fig. 13.

f (Hz)	<i>B</i> ₁	<i>B</i> ₂
200 240 280 400	$\begin{array}{rrrr} 8.4 \ \times \ 10^{-4} \\ 2.6 \ \times \ 10^{-4} \\ 8.7 \ \times \ 10^{-4} \\ 6.9 \ \times \ 10^{-4} \end{array}$	0.0183 0.0672 0.0918 0.1376

should mention that no data presented here was obtained at amplitudes for which the capillary waves broke up into droplets, or entrained bubbles.

IV. DISCUSSION

In this work capillary waves were generated via the Faraday instability so that a controllable, standing wave field could be investigated. The wave slope was varied, and it was found that K was linearly related to the mean-square wave slope.

Perhaps the most interesting result of this work concerns the magnitude of the values of K which were observed. Referring to Fig. 9, the magnitude of K is on the order of 0.01 cm/s for the f = 400 Hz data set. In fact, referring to Fig. 13, K exceeds 0.01 cm/s for both the f = 280 Hz and f = 400 Hz data sets. These values are put in perspective by comparison with wind/wave tunnel experiments. The data of Ocampo-Torres,¹ plotted in Fig. 1, show that K does not exceed 0.01 cm/s until the wind velocity exceeds 10 m/s. Hence in our experiments, capillary waves transfer CO₂ at a rate which is comparable to that which would occur in a wind/wave tunnel facility at a wind speed of 10 m/s. Obviously, the capillary waves which we have generated in our facility may differ from those which are observed in a wind/ wave tunnel, or on the open sea (i.e., parasitic capillary waves). Also, the water surface in our tank was completely covered with capillary waves, while this is not the case on the ocean. Nevertheless, our results do demonstrate that capillary waves have the potential to transport dissolved gases at a very high rate. Furthermore, since the wavelengths of the waves which we have investigated are comparable to those of typical parasitic capillary waves, it is very possible that regions of the ocean surface populated by parasitic capillary waves represent localized regions of very high flux and that a remote sensing method for measuring wave slope could also be used to locate regions of high heat or mass flux.

In addition to the magnitude of *K*, its variation is also of interest. Figure 9 shows that *K* increases with increasing wave slope and with decreasing wavelength (increasing frequency). The wavelength dependence will be addressed first. Referring again to Fig. 9, at constant wave slope, *K* increases rapidly with a decrease in λ . For example, at a constant slope of \overline{S} =0.15 m/m, *K* increases from 0.001 to 0.004 cm/s as λ decreases from 3.6 to 2.3 mm. Hence decreasing the wavelength by a factor of 1.6 results in a fourfold increase in transport. This is an intriguing result since wind/wave tunnel experiments typically show good correlation between mass transfer coefficient and wave slope in spite of the fact that many different wavelengths are present. The results pre-



FIG. 14. Plot of $\log(K)$ versus \overline{S} . The solid square symbol at zero wave slope corresponds to data taken with the electrodynamical shaker turned off.

sented here show good correlation with wave slope also, but only at constant wavelength. Exactly why transport varies so dramatically with wavelength at a constant wave slope is not clear at present. It is possible that the drift velocities which occur on the wave surface (and are discussed in more detail below), become more vigorous as the wavelength decreases (frequency increases). Actual velocity fields, obtained beneath the surface of these waves, are necessary to determine whether or not this is the case. An experimental program to obtain these measurements is currently being planned.

Another notable result of this work is the degree to which the capillary waves enhance transport over that of a flat surface. To illustrate this point the data of Fig. 9 is replotted, on semilogarithmic coordinates, in Fig. 14. The point having zero wave slope in this plot, was obtained by simply taking data with the shaker turned off. The value of K for this point is slightly greater than 1.0×10^{-4} cm/s, while the largest value of K for all of the data falls just below 0.01 cm/s, giving a range in K slightly less than two orders of magnitude. Actually, if the "off-detector" runs (see Fig. 13) were included, the range in K is greater than two orders of magnitude. Note that the zero excitation point does not correspond to pure diffusive mass transfer, since there are inevitably buoyancy driven flows due to natural convection in the tank.

The observed enhancement of two orders of magnitude exceeds the experimental data of MacIntyre,¹¹ as well as the analytical predictions of Szeri⁸ and Witting¹⁰ for the enhancement of transport due to capillary waves. As mentioned above, the exact mechanism for this large increase in K is not clear, however, some statements about what is occurring can, nonetheless, be made.

It should first be noted that while there is an increase in the transport of CO_2 due to increased surface area created by the waves, this can only explain a small portion of the observed increase in *K*. Because the wave profiles were not measured, the exact increase in surface area due to the waves was not computed. However, an upper bound on the increase in the surface area of the waves can be computed using the maximum peak-to-trough wave height of 1 mm and assuming the wave surface takes the form of two-dimensional step functions. Such a surface has an area larger than that which any capillary wave could create. The area A_e , of a surface, λ on a side, populated by these "step function waves" is given by the relation

$$A_e = \lambda^2 + 4a\lambda, \tag{19}$$

where *a* is the peak-to-trough amplitude of the wave. A patch of undisturbed surface, λ on a side, will have an area of

$$A = \lambda^2. \tag{20}$$

The increase in the surface area over that of the flat surface is defined by the variable F,

$$F = A_e / A. \tag{21}$$

Substituting Eqs. (19) and (20) into Eq. (21) gives

$$F = 1 + 4a/\lambda^2. \tag{22}$$

For a fixed value of *a* (1 mm in this case), *F* will be a maximum for the smallest value of λ . Referring to Table I, the smallest wavelength for these experiments is $\lambda = 2.26$ mm. Substituting this into Eq. (22) gives *F* = 2.8 meaning that the surface area is increased by, at most, a factor of 2.8. While this is a large increase (certainly larger than the increase in surface area that the waves in these experiments actually produced), it does not explain the two orders of magnitude increase in *K* which was observed.

A possible explanation concerns the drift velocities which occur on the surface of these capillary waves. As noted by Ramshankar et al.,²⁶ while a perfect standing wave has an extremely small drift velocity, even a very small spatial modulation in the standing wave pattern can result in significant surface drift velocities. These authors show that the surface velocities are random and have speeds on the order of several mm/s under conditions not dissimilar from those of the current work. Flow visualization experiments conducted by the present authors qualitatively confirmed the results of Ramshankar et al.²⁶ By placing a drop of dye on the water surface, extremely rapid mixing in the horizontal direction was observed. It is natural to expect that these random surface velocities will combine to form points of stagnation and divergence at various regions on the surface. These regions would act to exchange the surface fluid with the bulk. While we were unable to prove or disprove this point, we did note that when dye was injected beneath the water surface, bulk mixing, while small, did occur at a rate which was larger than that which was observed in the absence of waves. Because waves generate velocities which become negligibly small just one or two wavelengths beneath the water surface, it is reasonable to suggest that this bulk mixing is a result of the random surface velocities combining to create hydrodynamic currents which exchange surface fluid with the bulk. The velocities at which the dye was convected beneath the surface were much smaller than the surface velocities. Nevertheless, it is likely that this slow mixing contributed to CO₂ transport.

If the spatial modulation of the capillary wave field is indeed creating some sort of bulk fluid motion, then part of the increase in K which was observed may be due to the way in which we make our comparisons. In the work of Szeri,³ for example, two comparisons are made. One comparison is between pure capillary waves and pure diffusion, yielding a maximum increase in transport of about 3. Then Szeri⁸ presents a modified version of surface renewal theory, where a surface experiencing surface renewal in conjunction with capillary waves is compared to a surface experiencing surface renewal alone. In this case the capillary waves are shown to enhance transport by a maximum of 1.7. In our experiments, we are comparing a surface with waves and some degree of induced bulk mixing to a surface without waves and negligible bulk mixing (natural convection only). This comparison is not inappropriate, since whatever currents are formed by the waves are part of the inherent physics of these capillary waves. However, it should be noted that our comparison is, strictly speaking, not the same as that of Szeri⁸ and Witting.¹⁰ We are unable to make a similar comparison since our "bulk mixing" is caused by the waves themselves and can therefore never be eliminated. If we had included some artificial bulk motion, such as the stirring which MacIntyre¹¹ includes, the increase in K for a wavy surface with stirring over that for just a stirred system, would likely have been smaller than what is reported here.

Finally, although detailed measurements of the wave heights were not made, a comparison with the work of Crapper⁹ yields a rough estimate of the magnitude of the wave heights for this work. By differentiating Crapper's analytical solution to obtain slope, and then integrating, the average wave slope for Crapper waves $\overline{S_c}$ is obtained as

$$\overline{S_c} = 2\left\{\frac{1-A^2}{\pi Ab}\arctan\left(\frac{1}{b}\right)\right\},\tag{23}$$

where

$$A = \frac{2\lambda}{\pi a} \left\{ \left(1 + \frac{\pi^2 a^2}{4\lambda^2} \right)^{1/2} - 1 \right\},\tag{24}$$

$$b = \sqrt{\frac{1 + A^4 - 6A^2}{4A^2}},\tag{25}$$

and *a* is the peak-to-trough wave amplitude. The values of \overline{S} for the current experiments varied from zero to just above 0.2 m/m. In Fig. 15 four plots of the wave profiles obtained from the solution due to Crapper⁹ are presented. Each profile corresponds to a value of the parameter a/λ , chosen so that the average wave slope for that profile corresponded to $\overline{S_c} = 0.05, 0.10, 0.15, \text{ and } 0.2 \text{ m/m}$, thereby spanning the range of \overline{S} explored in this work. The largest wave height shown in these plots has an amplitude of $a/\lambda = 0.099$. This value corresponds to a height of a = 0.36 mm (for the largest wavelength), not very different from our crudely measured value of 1 mm. Since a/λ must exceed 0.73 before bubbles or droplets are formed, the above result indicates that a great deal of mass transfer can be obtained even at relatively low wave slopes.

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FIG. 15. Profiles of Crapper waves for four selected values of $\overline{S_c}$. (a) $\overline{S_c} = 0.05 \text{ m/m}$, (b) $\overline{S_c} = 0.10 \text{ m/m}$, (c) $\overline{S_c} = 0.15 \text{ m/m}$, and (d) $\overline{S_c} = 0.20$. These four values correspond to $a/\lambda = 0.025$, 0.050, 0.074, and 0.099, respectively.

V. CONCLUSION

Experiments on gas transport across an air/water interface populated by capillary waves were presented. Faraday waves were used as a platform for investigating how capillary waves affect transport in a controllable laboratory setting, where such complicating factors as turbulence and aerosol formation were eliminated. The average wave slope varied from 0 to about 0.2 m/m. It was demonstrated that mass transfer coefficients as large as K = 0.01 cm/s were obtained for average wave slopes of order 0.2 m/m. Such large mass transfer coefficients are typically obtained in a wind/ water tunnel only when the wind speed exceeds 10 m/s. These results indicate that capillary waves have the potential to transport a large amount of dissolved gas (and presumably heat), raising the question of exactly how much transport on the open sea is due to capillary waves. While an exact explanation for the mechanism by which transport is effected by these waves is left for future work, it is suggested that the random surface drift velocities observed in this system may act to generate some degree of bulk mixing. Measurements of the velocity field below a capillary wave surface are necessary to determine the exact mechanism of the enhanced transport which was observed herein.

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