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Raman spectroscopy of solutions and interfaces containing nitrogen dioxide, water, and 1,4 dioxane: Evidence for repulsion of surface water by NO$_2$ gas

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The interaction of water, 1,4 dioxane, and gaseous nitrogen dioxide, has been studied as a function of distance measured through the liquid-vapour interface by Raman spectroscopy with a narrow (<0.1 mm) laser beam directed parallel to the interface. The Raman spectra show that water is present at the surface of a dioxane-water mixture when gaseous NO$_2$ is absent, but is virtually absent from the surface of a dioxane-water mixture when gaseous NO$_2$ is present. This is consistent with recent theoretical calculations that show NO$_2$ to be mildly hydrophobic. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Kolb et al.$^1$ have presented a thorough review, up to 2010, of outstanding theoretical and experimental problems relating to the reactions of atmospheric trace gases, including NO$_2$, with a variety of wet and dry surfaces, and it is clear that there are still many interesting problems that need to be investigated.

A recent theoretical study$^2$ of the interaction of nitrogen dioxide with the surface of water led to the conclusion that, even though the binding energy of the O$_2$N–OH$_2$ complex was found to be 9.5 kJ mol$^{-1}$, a factor of 2 larger than previously calculated, nitrogen dioxide is at least “mildly” hydrophobic. Instead of taking part in hydrogen bonds, the oxygen atoms of NO$_2$ were found to be repelled by water molecules, which led to an unexpected preferential orientation of NO$_2$ at the surface, with the oxygen atoms pointing out of the interface, and suggested that, in a system with mixed solvents, the surface might actually be depleted of water. This cast new light on the processes by which nitrous acid (HONO) is produced in the troposphere, indicated the need for recent theoretical calculations that show NO$_2$ to be mildly hydrophobic.

The experiments reported here do not require surface selectivity of the kind employed in the experiments of Donaldson et al.$^3$–$^8$ but simply exploit the ability of Raman spectroscopy with a narrow (<0.1 mm) laser beam to obtain spectra that arise from species close to and within the interface. This limited selectivity, perhaps somewhat unexpectedly, proves to be sufficient to detect the mutual repulsion between water molecules and NO$_2$ molecules at the gas-liquid interface. To make the experiment work, it was necessary to use a mixed solvent comprised of water and 1,4 dioxane, the purpose of the dioxane being to provide a reference surface relative to which the displacement of water could be observed.

Surface tension measurements$^9$ indicate that 1,4 dioxane behaves as a weak surfactant in water, but this surfactant effect plays no role in our experiments, which could not resolve a surface monolayer. Dioxane was chosen as the reference substance because it is both unreactive and totally miscible with water, properties that have often been exploited by electrochemists and spectroscopists.

As in the earlier study of NO$_2$ gas interacting with nitric acid,$^{10}$ Raman spectra of H$_2$O.NO$_2$ species were sought but, consistent with the theoretical prediction of very weak binding between H$_2$O and NO$_2$, and the small calculated frequency differences between the vibrations of unbound and bound species (Table I), no such spectra were found. The absence of large red shifts in the IR upon formation of the NO$_2$–H$_2$O complex is another indication that normal hydrogen bonds are not formed, but rather the relatively weaker and longer bonds discussed in Ref. 2.

Low-resolution fluorescence spectra of gaseous NO$_2$ were observed with comparable intensity to the Raman spectra. The long (100 µs) radiative lifetime$^{11}$ of NO$_2$ at the excitation wavelength (523 nm) used in our experiments caused the fluorescence spectrum of NO$_2$ gas excited close to the interface to be distinctly different from that of gas excited only

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TABLE I. Calculated vibrational frequencies (harmonic, unscaled, using BLYP-D2/aug-cc-pVDZ, see Ref. 2 for details) for NO$_2$ and H$_2$O and for two isomers of the H$_2$O.NO$_2$ complex. Experimental frequencies for NO$_2$ and H$_2$O are also shown.

|      | NO$_2$ calc. | H$_2$O calc. |      | NO$_2$ expt. | H$_2$O expt. |
|------|--------------|---------------|------|--------------|--------------|
|      | 753 1393 1704 | 1616 3791 3903 |      | 750 1318 1618 | 1595 3657 3756 |
| Cs H$_2$O.NO$_2$ calc. | 754 1398 1712 | 1610 3792 3906 | Cs H$_2$O.NO$_2$ calc. | 754 1396 1707 | 1610 3789 3903 |
| C$_2$v H$_2$O.NO$_2$ calc. | 754 1396 1707 | 1610 3789 3903 |      | C$_2$v H$_2$O.NO$_2$ calc. | 754 1396 1707 | 1610 3789 3903 |

where everyone of these reversible processes involves some interesting dynamics. In our system, the resonance Raman spectrum of NO$_2$ is about 150 times more intense than the non-resonance Raman spectrum of N$_2$O. The N$_2$O peak at 2223.5 cm$^{-1}$ is overlapped by a fluorescence band of NO$_2$ but could be observed when the NO$_2$ concentration, as indicated by the intensity of the blue colour of the frozen sample, was low.

II. EXPERIMENTAL

The Raman spectrometer and sample cell were the same as before$^{10}$ except that, on the viewing window of the cell, the curved parts of the meniscus where it met the windows at right angles to the viewing window were obscured by narrow, vertical strips of metal foil glued onto the outside of the cell, and a Dove prism was inserted into the optical system for collecting scattered light, in order to rotate the horizontal green image of the laser-irradiated solution to match the vertical spectrometer slit. Otherwise the laser diode, notch filter, spectrometer, and CCD detector were as previously described. All of the experiments reported here used a spec-
exposure time, so that the intensity values indicated along the vertical axes of the graphs are significant. The sample cell was mounted on a micrometer-driven platform that enabled the vertical separation of the laser beam from the liquid surface to be adjusted reproducibly to within about 0.01 mm. The calculated beam waist within the cell was less than 0.1 mm in diameter but, because the beam intensity profile is expected to be Gaussian, the effective spatial resolution of the Raman scattering was somewhat greater than this. As a result, spectra taken at 0.1 mm intervals were slightly contaminated with spectra from adjacent 0.1 mm steps. This contamination was not fatal to our objective, which was to compare the surface distributions of water and 1,4 dioxane in the presence and absence of NO₂. Many of the spectra, especially those with long exposure times, were also affected by “cosmic-ray spikes.” The spikes, which were almost invariably positive-going and seldom more than 3 pixels wide, were removed by hand, using a computer program written in Chipmunk Basic.

A mixture of spectroscopic grade 1,4 dioxane with milli-Q water, of known composition by volume, was degassed in the side-arm of the cell by a series of freeze-pump-thaw cycles. For most of the experiments, the mixture comprised equal volumes of the two liquids. An equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide was prepared by adding a large excess of oxygen to nitric oxide that had been purified by trap-to-trap distillation. The mixture was left overnight before trapping the NO₂/N₂O₄ as a white solid at liquid nitrogen temperature and pumping off the excess oxygen. The resulting bulb of gas at a pressure of a few hundred torr was used to introduce NO₂/N₂O₄ into the cooled side-arm of the cell until the frozen solid was a more-or-less intense dark blue. Most of the spectra shown here were obtained with dark blue samples. The side-arm was then shut off from the vacuum system, the solid was allowed to thaw, and the cell was shaken well before being transferred to the micrometer-driven platform, where it remained for up to a week while spectra were being taken. Measurements made at intervals of several days were in excellent agreement, which implies that any observed depletion of water in the surface layer was not merely the result of slow dissolving of NO₂ from the gas phase.

III. RESULTS AND DISCUSSION

The aim of these experiments was to determine whether the presence of NO₂ gas above the interface affected the concentration of H₂O at the interface. As a first step, we needed to obtain Raman spectra of pure 1,4 dioxane and of a dioxane-water mixture in our system, as shown in Figs. 2(a) and 2(b), respectively, and of dioxane vapour very close to the surface, as shown in Fig. 2(c). The water peak at 3400 cm⁻¹ is a distinctive feature of Fig. 2(b).

The next step was to obtain Raman spectra in the 3400 cm⁻¹ region for a 1:1 water-dioxane mixture, without NO₂, at a series of heights that included the interface. Typical spectra are shown in Figs. 3(a)–3(f), with the beam height in mm indicated on each graph, the height increasing as the laser beam rose through the interface. The dioxane peak intensity decreased by a factor of ten as the beam height rose from 6.0 to 6.6 mm, and the water peak was still present at 6.6 mm. At 6.7 mm and above, a comparison with Fig. 2(c) reveals that much of the remaining dioxane peak was due to dioxane.

FIG. 2. (a) Part of the Raman spectrum of pure 1,4 dioxane. (b) Raman spectrum of a 1:1 mixture of water and 1,4 dioxane. (c) Raman spectrum of dioxane vapour near the liquid surface, with no NO₂ present.

FIG. 3. Raman spectra of a 1:1 mixture of water and 1,4 dioxane at various beam heights.
vapour, so we can conclude that, in the absence of NO₂, there is no evidence for a marked decrease in the water concentration relative to dioxane as the beam moves up through the interface. This shows incidentally that, with a height resolution of the order of 0.05 mm, the surfactant nature of dioxane in dioxane-water mixtures did not result in significant exclusion of water from the surface of the mixed solvent. This is expected, because such behaviour should result in the formation of a monolayer, which would not be detectable in our experiments.

Next, we examined the effect of moving the laser beam up through the interface for a cell containing water, dioxane,
and NO₂, looking first at the 1300 cm⁻¹ region. Typical spectra are shown in Figs. 4(a)–4(c). The height scale does not correspond precisely to that in Fig. 3 because the cell had to be moved to the vacuum system to introduce the NO₂ and then back again, but the height scales in Figs. 4 and 5 do correspond exactly. The spectrum in Fig. 4(a) is similar to that in Fig. 1(c), showing mainly dioxane peaks with almost no NO₂ gas. Small, gas-like NO₂ and NO peaks are to be expected from the liquid because, in the 1:1 solvent mixture, some of the NO₂ and NO molecules will be surrounded by solvent shells composed entirely of dioxane. The peaks of NO₂ gradually increase and those of dioxane decrease as the beam moves upward, and it appears that the interface is located at a beam height of about 8.6 mm.

The plots in Figs. 5(a)–5(c), for the 3400 cm⁻¹ region show, in addition to the composite dioxane peak, a change from a small water peak with superimposed NO₂ bands at a height of 8.5 mm, to the spectrum of NO₂ gas close to the liquid surface at a height of about 8.7 mm. The plot of Fig. 5(b), at the level of 8.6 mm that we now assign to the interface region, appears to consist of a dioxane peak adjoining the NO₂ fluorescence of Fig. 1(a), with no sign of the water peak at 3400 cm⁻¹. The plot in Fig. 5(d) is intended to make this point more obvious. The portion of the plot that is identical with Fig. 5(b) is overlaid quite neatly by the scaled NO₂ fluorescence spectrum of Fig. 1(a) in the 3400 cm⁻¹ region. The plot of Fig. 5(a) has been scaled to fit the dioxane peak of Fig. 2(a) between 2800 and 3000 cm⁻¹, where it too fits well. However, the 3400 cm⁻¹ water peak of Fig. 2(b) is not able to be accommodated anywhere. Hence it appears that, in the presence of NO₂, the surface layer of liquid is strongly depleted of water.
IV. CONCLUSIONS

The mutual repulsion of water and NO$_2$, which occurs at the molecular level, has been found to have significant consequences on a macroscopic scale at the surface of a blue solution of 1,4 dioxane and water in the presence of gaseous NO$_2$. The thickness of the relevant surface layer is of the order of 0.05 mm, which is much greater than the thickness of the region probed by grazing-incidence Raman spectroscopy. This possibly surprising observation depends critically on the total miscibility and lack of mutual reactivity of the dissimilar solvents 1,4 dioxane and water, which permit the surface layer to become depleted of water in the presence of NO$_2$ gas. Thus, the present paper supports the theoretical conclusion$^1$ that direct formation of HONO from water and NO$_2$ under atmospheric conditions is not a facile process, because water and gas-phase NO$_2$ tend to repel one another in the surface region. It might also be regarding as providing indirect support for the suggestion$^{14}$ that the formation of atmospheric HONO could involve NO$_2^-$ ions formed by electron capture by NO$_2$ from electrically charged surfaces.

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