

UC Irvine

UC Irvine Previously Published Works

Title

Raman spectroscopy of solutions and interfaces containing nitrogen dioxide, water, and 1,4 dioxane: Evidence for repulsion of surface water by NO₂ gas

Permalink

<https://escholarship.org/uc/item/7t6098n9>

Journal

The Journal of Chemical Physics, 140(18)

ISSN

0021-9606

Authors

Murdachaew, Garold
Varner, Mychel E
van der Veer, Wytze E
[et al.](#)

Publication Date

2014-05-14

DOI

10.1063/1.4874640

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Raman spectroscopy of solutions and interfaces containing nitrogen dioxide, water, and 1,4 dioxane: Evidence for repulsion of surface water by NO₂ gas

Garold Murdachaew,¹ Mychel E. Varner,² Wytze E. van der Veer,² R. Benny Gerber,^{1,2} and Leon F. Phillips^{2,3,a)}

¹*Institute of Chemistry and the Fritz Haber Research Center for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel*

²*Department of Chemistry, University of California, Irvine, California 92697, USA*

³*Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand*

(Received 26 November 2013; accepted 21 April 2014; published online 8 May 2014)

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 NO₂ is absent, but is virtually absent from the surface of a dioxane-water mixture when gaseous NO₂ is present. This is consistent with recent theoretical calculations that show NO₂ to be mildly hydrophobic. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4874640>]

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 NO₂, 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 study² of the interaction of nitrogen dioxide with the surface of water led to the conclusion that, even though the binding energy of the O₂N–OH₂ 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 NO₂ were found to be repelled by water molecules, which led to an unexpected preferential orientation of NO₂ 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 an experimental test of the theoretical results, and provided the motivation for the present study.

Donaldson and co-workers^{3–8} have shown that glancing-angle Raman spectroscopy is a very useful surface-selective technique for probing a surface region with a thickness of the order of 10–100 molecular layers, being able to measure both surface concentrations of solutes and surface depletion of solvents. Thus, for example, Wren and Donaldson⁷ used glancing-angle Raman spectroscopy to study the reaction of gas-phase ozone with NaBr and NaI at the surfaces of aqueous solutions.

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 NO₂ 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 measurements⁹ 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 NO₂ gas interacting with nitric acid,¹⁰ Raman spectra of H₂O·NO₂ species were sought but, consistent with the theoretical prediction of very weak binding between H₂O and NO₂ 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 NO₂–H₂O complex is another indication that normal hydrogen bonds are not formed, but rather the relatively weaker and longer bonds discussed in Ref. 2.

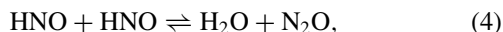
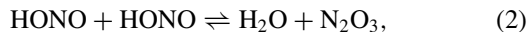
Low-resolution fluorescence spectra of gaseous NO₂ were observed with comparable intensity to the Raman spectra. The long (100 μs) radiative lifetime¹¹ of NO₂ at the excitation wavelength (523 nm) used in our experiments caused the fluorescence spectrum of NO₂ gas excited close to the interface to be distinctly different from that of gas excited only

^{a)} Author to whom correspondence should be addressed. Electronic mail: leon.phillips@canterbury.ac.nz

TABLE I. Calculated vibrational frequencies (harmonic, unscaled, using BLYP-D2/aug-cc-pVDZ, see Ref. 2 for details) for NO₂ and H₂O and for two isomers of the H₂O.NO₂ complex. Experimental frequencies for NO₂ and H₂O are also shown.

NO ₂ calc.			H ₂ O calc.		
753	1393	1704	1616	3791	3903
C _s H ₂ O.NO ₂ calc.			C _s H ₂ O.NO ₂ calc.		
754	1398	1712	1610	3792	3906
C _{2v} H ₂ O.NO ₂ calc.			C _{2v} H ₂ O.NO ₂ calc.		
754	1396	1707	1610	3789	3903
NO ₂ expt.			H ₂ O expt.		
750	1318	1618	1595	3657	3756

a few millimeters higher in the cell (Figs. 1(a) and 1(b)). The low-wavenumber Raman spectrum of the bulk solution several millimeters below the interface (Fig. 1(c)) showed peaks that could be assigned to HNO₃, HNO₂, N₂O₄, N₂O₃, NO₂, NO, N₂O, nitrite and nitrate ions, as well as dioxane. The odd members of this collection are NO, formed by decomposition of N₂O₃, N₂O₃, which is responsible for the blue colour of the solution, and N₂O (not shown in Fig. 1(c)), for which a plausible production mechanism¹² is



where everyone of these reversible processes involves some interesting dynamics. In our system, the resonance Raman spectrum of NO₂ is about 150 times more intense than the non-resonance Raman spectrum of N₂O. The N₂O peak at 2223.5 cm⁻¹ is overlapped by a fluorescence band of NO₂ but could be observed when the NO₂ 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 before¹⁰ 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-

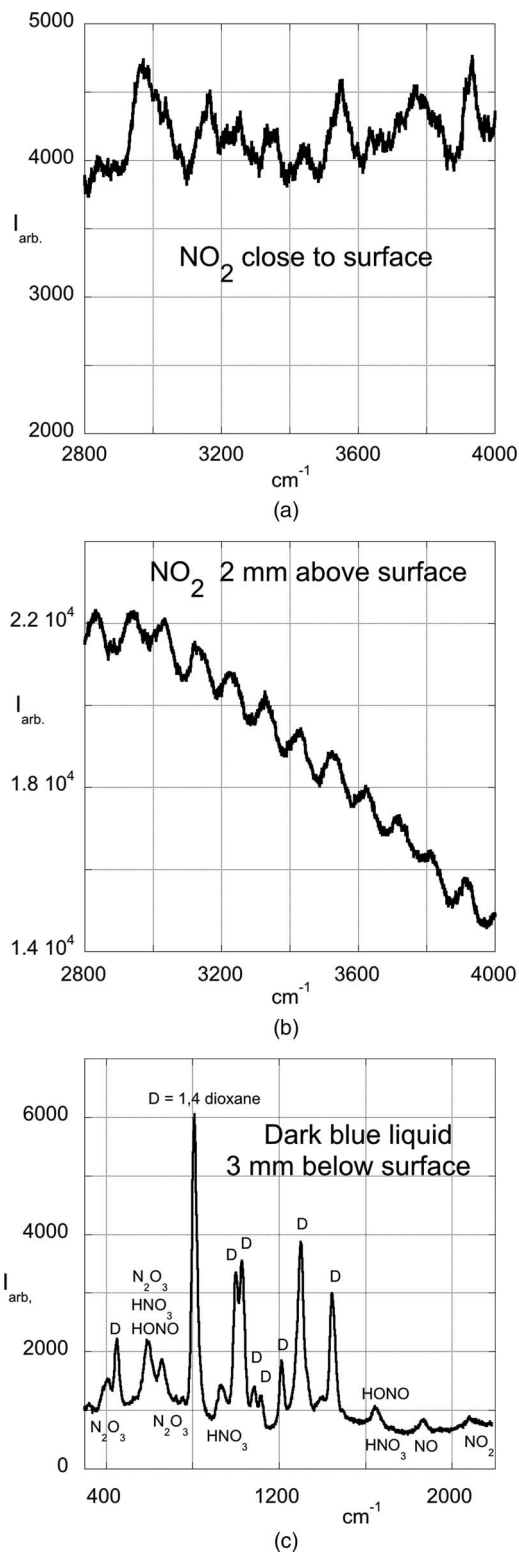


FIG. 1. (a) Fluorescence spectrum of NO₂ measured close to the liquid surface (<0.5 mm away). The wave-number scale indicates displacement from the 523 nm exciting line. (b) Fluorescence spectrum of NO₂ measured ~2 mm above the liquid surface. The wave-number scale indicates displacement from the 523 nm exciting line. (c) Raman spectrum of a blue solution of NO₂ in a 20:80 (by volume) mixture of water and 1,4 dioxane, showing the detectable components below 2200 cm⁻¹.

trometer slit width of 0.25 mm. Exposure times varied between 15 and 180 s, and Raman intensities, plotted in arbitrary units in the graphs that follow, were scaled inversely with

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 NO_2 . 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.¹³

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 $\text{NO}_2/\text{N}_2\text{O}_4$ 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 $\text{NO}_2/\text{N}_2\text{O}_4$ 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 NO_2 from the gas phase.

III. RESULTS AND DISCUSSION

The aim of these experiments was to determine whether the presence of NO_2 gas above the interface affected the concentration of H_2O 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 NO_2 , 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

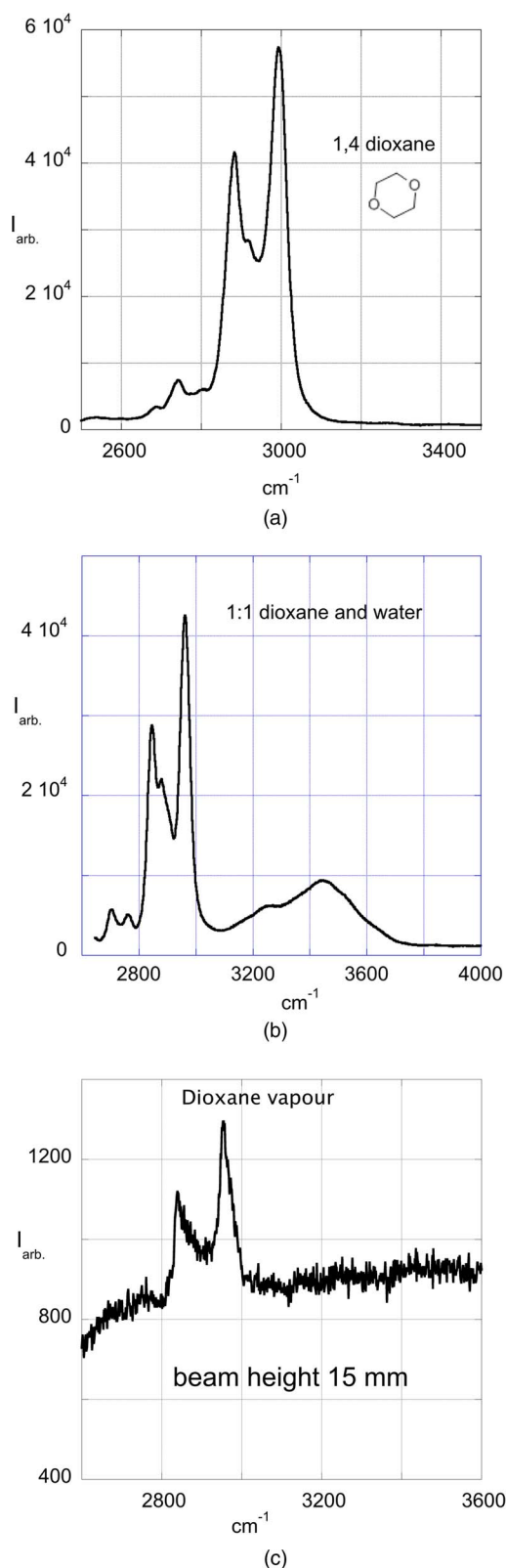


FIG. 2. (a) Part of the Raman spectrum of pure 1,4 dioxane. (b) Raman spectrum of a 1:1 mixture of water and 1,4 dioxane. (c) Raman spectrum of dioxane vapour near the liquid surface, with no NO_2 present.

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

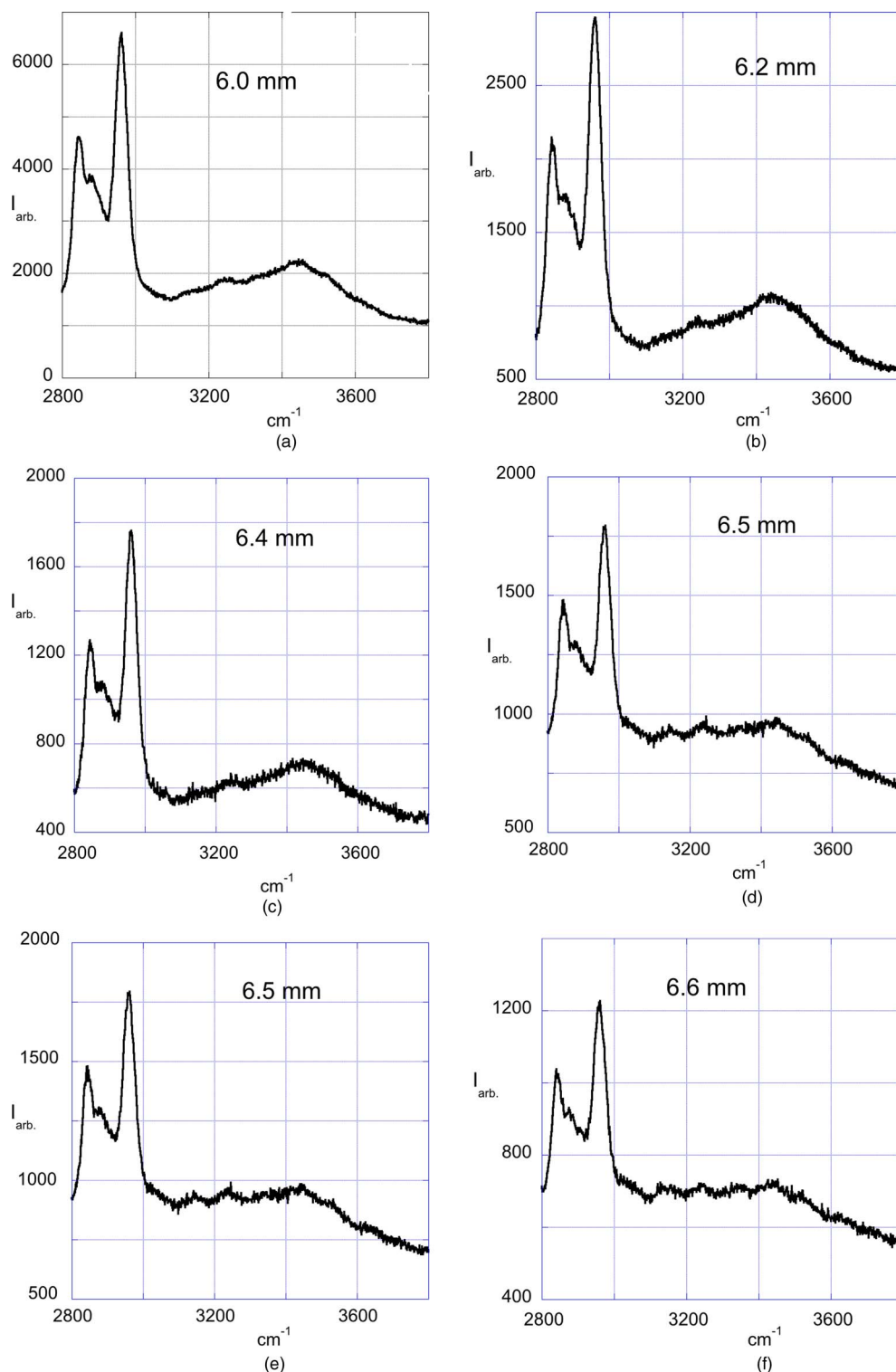


FIG. 3. (a)–(f) Raman spectra of a 1:1 by volume mixture of water and 1,4-dioxane, with no NO_2 , as a function of the height of the laser beam. The height of the surface is between 6.4 and 6.6 mm and water is present all the way to the surface.

vapour, so we can conclude that, in the absence of NO_2 , 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 exclu-

sion 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,

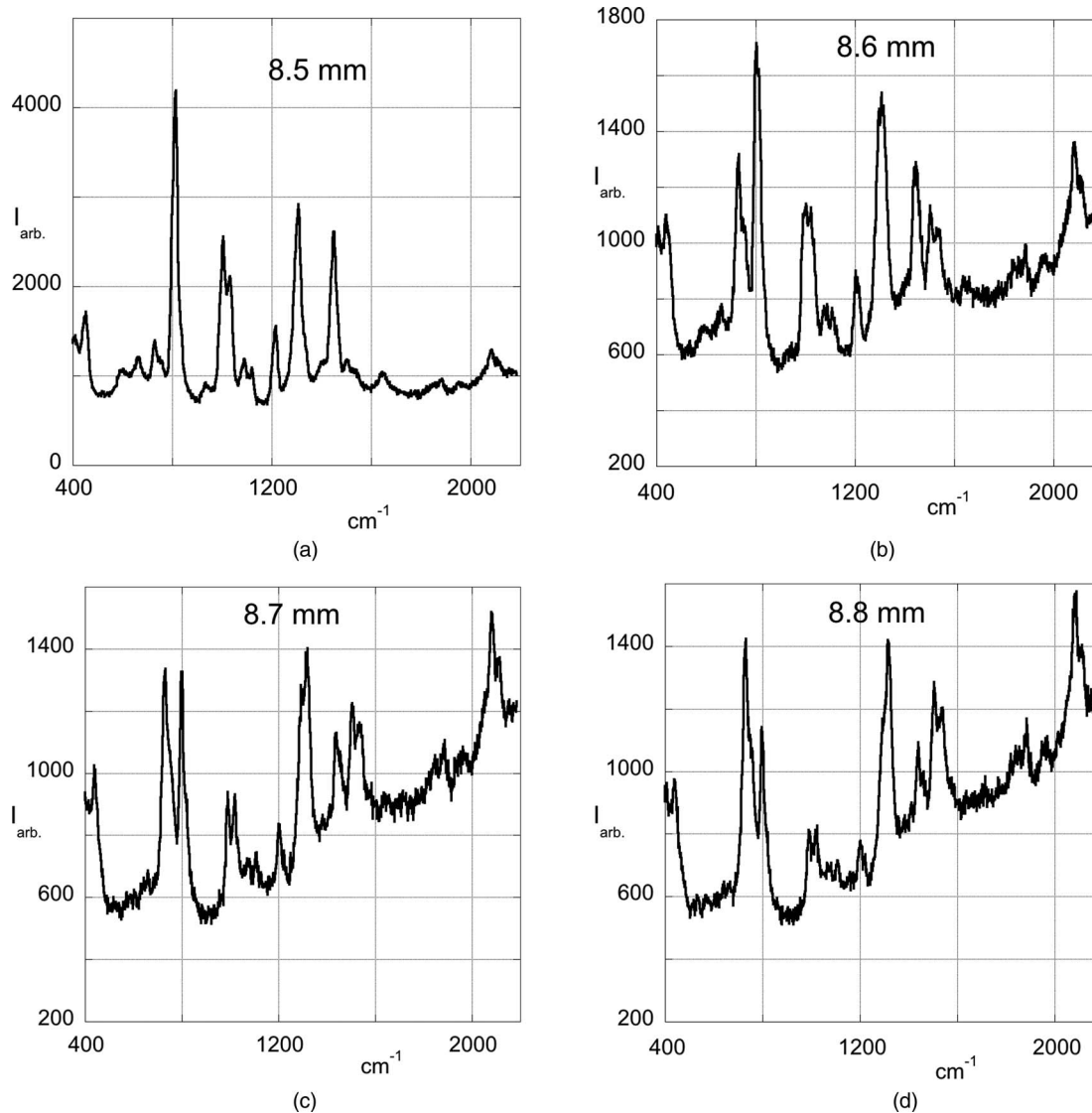


FIG. 4. (a)–(d) Low wave-number Raman spectrum of a 1:1 (by volume) mixture of water and 1,4 dioxane in the presence of NO_2 , as a function of the height of the laser beam. As the beam height increases the dioxane peaks diminish and the NO_2 peaks and fluorescence background increase. The height of the liquid surface is about 8.6 mm. Peak assignments for Fig. 4(a) are the same as in Fig. 1(c), with minor differences due to the differing solvent composition.

and NO_2 , 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 NO_2 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 NO_2 gas. Small, gas-like NO_2 and NO peaks are to be expected from the liquid because, in the 1:1 solvent mixture, some of the NO_2 and NO molecules will be surrounded by solvent shells composed entirely of dioxane. The peaks of NO_2 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 NO_2 bands at a height of 8.5 mm, to the spectrum of NO_2 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 NO_2 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 NO_2 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 NO_2 , the surface layer of liquid is strongly depleted of water.

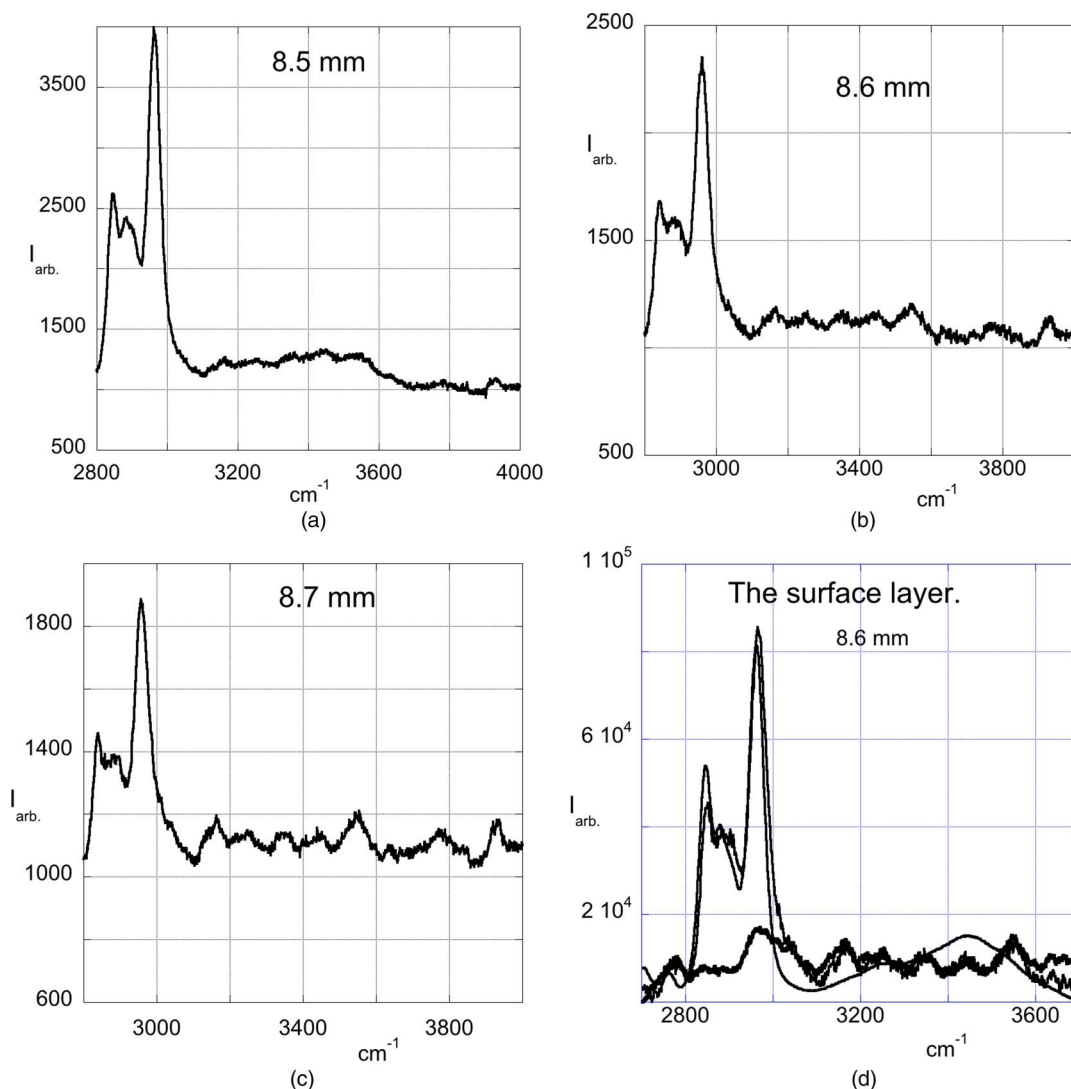


FIG. 5. (a)–(c) As in Fig. 4, but observing in the region of the water peak at 3400 cm^{-1} . The spectrum in Fig. 5(a) shows the dioxane peak and the water peak with weak NO_2 fluorescence superimposed on the water peak. The spectrum obtained at a beam height of 8.6 mm shows the dioxane peak between 2800 and 3000 cm^{-1} and the NO_2 fluorescence close to the liquid surface, but the water peak at 3400 cm^{-1} is not evident above 8.5 mm. (d) The Raman spectrum of Fig. 5(b), analysed into the dioxane spectrum, plus NO_2 fluorescence. The water peak of Fig. 3(a) (shown by the relatively noise-free solid line) clearly is not present in Fig. 5(b).

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 conclusion¹ 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 regarded as providing indirect support for the suggestion¹⁴ that the formation of atmospheric HONO

could involve NO_2^- ions formed by electron capture by NO_2 from electrically charged surfaces.

ACKNOWLEDGMENTS

We are grateful to Professor Barbara Finlayson-Pitts for providing the environment and stimulus for this work, which was supported by Grant No. 0909227 from the United States National Science Foundation (NSF).

¹C. E. Kolb, R. A. Cox, J. P. D. Abbatt, M. Ammann, E. J. Davis, D. J. Donaldson, B. C. Garrett, C. George, P. T. Griffiths, D. R. Hanson, M. Kulmala, G. McFiggans, U. Pöschl, I. Riipinen, M. J. Rossi, Y. Rudich, P. E. Wagner, P. M. Winkler, D. R. Worsnop, and C. D. O' Dowd, *Atmos. Chem. Phys.* **10**, 10561–10605 (2010).

²G. Murdachaew, M. E. Varner, L. F. Phillips, B. J. Finlayson-Pitts, and R. B. Gerber, *Phys. Chem. Chem. Phys.* **15**, 204–212 (2013).

³T. F. Kahan, J. P. Reid, and D. J. Donaldson, *J. Phys. Chem.* **111**, 11006–11012 (2007).

⁴D. I. Reeser, A. Jammoul, D. Clifford, M. Brigante, B. D'Anna, C. George, and D. J. Donaldson, *J. Phys. Chem. C* **113**, 2071–2077 (2009).

- ⁵D. Clifford and D. J. Donaldson, *J. Phys. Chem. A* **111**, 9809–9814 (2007).
- ⁶T. F. Kahan and D. J. Donaldson, *J. Phys. Chem. A* **111**, 1277–1285 (2007).
- ⁷T. F. Kahan, N. O. A. Kwamena, and D. J. Donaldson, *Atmos. Environ.* **40**, 3448–3459 (2006).
- ⁸S. N. Wren and D. J. Donaldson, *Phys. Chem. Chem. Phys.* **12**, 2648–2664 (2010).
- ⁹F. Hovorka, R. A. Schaefer, and D. Dreisbach, *J. Am. Chem. Soc.* **58**, 2264–2267 (1936).
- ¹⁰M. A. Kamboures, W. E. van der Veer, R. B. Gerber, and L. F. Phillips, *Phys. Chem. Chem. Phys.* **10**, 4748–4753 (2008).
- ¹¹V. M. Donnelly and F. Kaufman, *J. Chem. Phys.* **69**, 1456–1460 (1978).
- ¹²B. J. Finlayson-Pitts, L. M. Wingen, A. L. Syomin, and K. Ramazan, *Phys. Chem. Chem. Phys.* **5**, 223–242 (2003).
- ¹³See www.nicholson.com/rhn/basic/ for Chipmunk Basic source files.
- ¹⁴L. F. Phillips, *Phys. Chem. Chem. Phys.* **15**, 10749–10752 (2013).