# Electronic Supplementary information

*The carbonate/bicarbonate system as a pH indicator for infrared spectroscopy*

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## Absorption spectra of sodium carbonate and bicarbonate in $^2H_2O$

The infrared absorption spectra of 100 mM carbonate/bicarbonate solutions at different $p^2H$ values are shown in Figure S1. A detailed analysis of the bands is given in the main text.
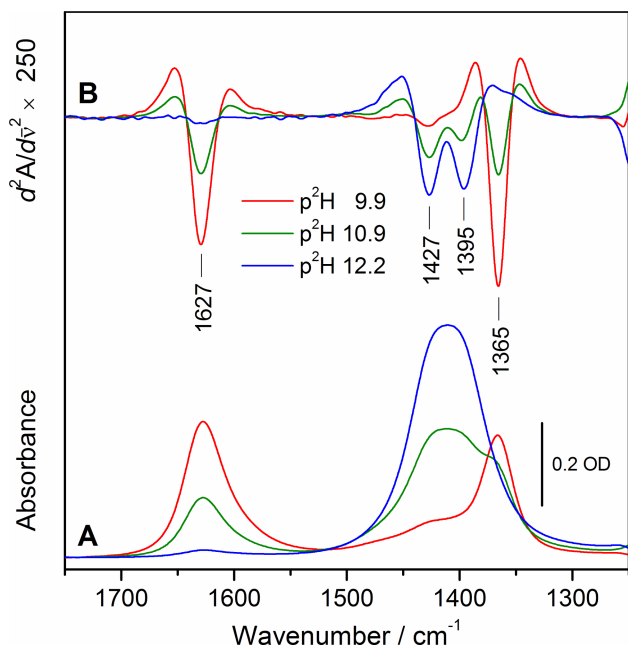


**Figure S1.** Absorption (A) and second derivative (B) spectra of 100 mM carbonate/bicarbonate in $^2H_2O$ medium at $p^2H$ 9.9 (red), 10.9 (green) and 12.2 (blue).

## Photolysis reaction of NPE-sulphate

The structure of NPE-sulphate, of the photolysis byproduct 2-nitrosoacetophenone and of the reaction intermediates in shown in Figure S2. UV illumination of NPE-sulfate (A) induces rearrangement to the primary photochemical product, a nitronic acid (B). This is in rapid equilibrium with its conjugate *aci*-nitro anion (C). The lifetime of this intermediate is inversely proportional to the concentration of protons and may be used, in some circumstances, to obtain information on the pH value reached after the flash. The protonated nitronic acid rearranges to intermediate (D) which breaks down to 2-nitrosoacetophenone (E) and free sulphate.
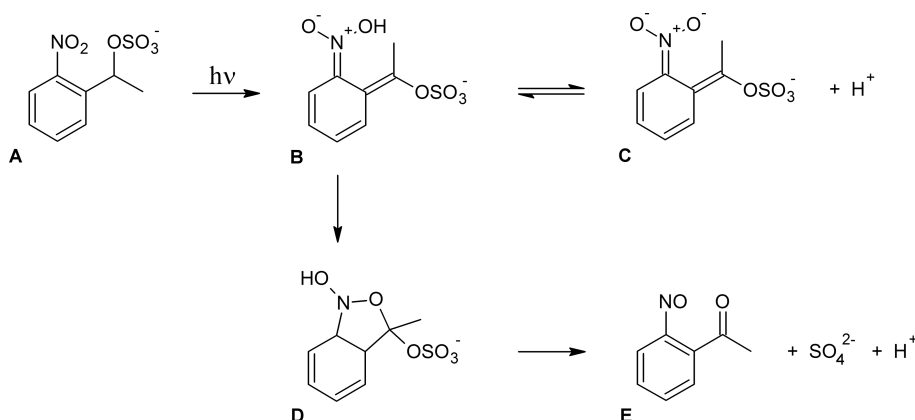


**Figure S2.** Structure and photolysis reaction mechanism of NPE-sulphate.

**Flash-photolysis experiments in the presence of 2 mM Na₂CO₃**

Figure S3 shows the difference spectrum obtained upon one single UV flash on 20 mM NPE-sulfate in the presence of 2 mM Na₂CO₃ after subtraction of the photolysis bands (black spectrum), and the corresponding fit (red spectrum). Analysis of the fitted spectrum by the algorithm yields the plot shown in panel D. The resulting peak is well defined in the $p^2H_i$ dimension ($p^2H_i = 11$), but the final $p^2H$ stretches from $p^2H$ 9.6 to 8. This occurs because the latter values lie in between the two $pK$ values, where the $p^2H$-depedent change in carbonate and bicarbonate concentration is at its minimum. It can be observed, however, that the initial $p^2H$ value is higher, and that the magnitude of the jump is more modest than in the experiment with 1 mM Na₂CO₃, which supports the reliability of our approach. An additional UV flash performed on the sample yields, after subtraction of the photolysis signals, the difference spectrum (black line) and the corresponding fit (red line) shown in panel B. Both spectra only show peaks arising from the disappearance of bicarbonate, thereby suggesting that the initial $p^2H$ is $<<$ $pK_2$ (10.97). Indeed, analysis of the fitted spectrum shows an arch-shaped peak centered at approximately ($p^2H_i = 8$; $p^2H_f = 5.8$). The uncertainty in both dimensions occurs because of the phenomenon described above. Nevertheless, the peak is relatively narrow and features a high $\rho$ score (29.10). Combining the difference spectra obtained upon both flashes (panel C) allows to confirm the $p^2H$ before the first flash, and the final $p^2H$ after the second flash. In this case, our approach gives a very narrow and well defined peak centered at ($p^2H_i = 11$; $p^2H_f = 5.8$). There is some degree of uncertainty in the $p^2H_f$ dimension which, however, appears to be lower than before. The initial $p^2H$ is, in contrast, well defined.
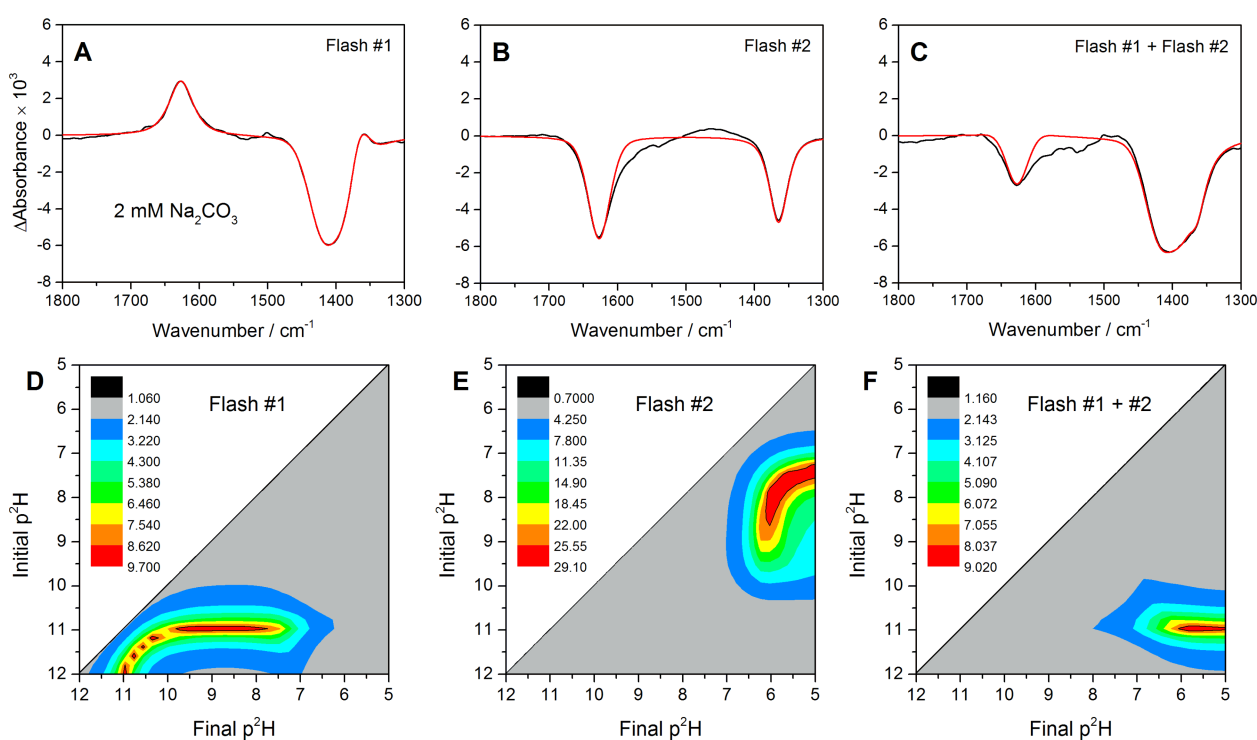


**Figure S3.** Analysis of difference spectra obtained in photolysis experiments of NPE-sulfate in the presence of 2 mM Na₂CO₃ in ²H₂O. (A) Experimental difference spectrum recorded after the first UV-flash in the presence Na₂CO₃, after subtraction of the photolysis signals (black line), and the corresponding fitted spectrum (red line). (B) As in A, after the second UV-flash. (C) Sum of the two experimental difference spectra in A and B (black line), and of the corresponding fits (red line). (D-F) Similarity score plots of the fitted spectra in panels A-C.