PAPER PRESENTATION

RESEARCH ARTICLES

PHYSICAL CHEMISTRY

Spontaneous formation of urea from carbon dioxide and ammonia in aqueous droplets

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Urea is a key molecule in the search for the origin of life and a basic chemical produced in large quantities by industry. Its formation from ammonia and carbon dioxide requires either high pressures and temperatures or, under milder conditions, catalysts or additional reagents. In this study, we observed the spontaneous formation of urea under ambient conditions from ammonia and carbon dioxide in the surface layer of aqueous droplets. Single, optically trapped droplets were probed by using Raman bands as markers. We found the surface layer to act like a microscopic flow reactor, with chemical gradients providing access to unconventional reaction pathways. This observation revealed a general mechanistic scheme for distinctive droplet chemistry. Interfacial chemistry is a possible nonenergetic route for urea formation under prebiotic conditions.

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Introduction

- Urea is a key molecule in the search for the **origin of life.**
- It plays a key role in the **amino acid metabolisms** of mammals and amphibians through the urea cycle, by which toxic ammonia is removed from the body.
- It is produced in larger quantities to be used primarily in the fertilizer industry along with production of resins and explosives.
- Urea is considered as a **fundamental building block** in the formation of biological molecules.
- The formation of urea in **CO_2 rich atmosphere** in the early prebiotic earth which also contained small amounts of ammonia has not yet been conclusively proven.

Why this paper?

- Industrially, the formation of urea requires either **high temperatures or pressures** or, under milder conditions it requires the **addition of catalysts or additional reagents.**
- Droplets based synthesis of urea molecule is important as it can be formed under ambient conditions with more sustainability and less energy demand.
- Single, optically trapped droplets study enabled showing the formation of urea by in-situ Raman bands as markers.
- It compared the **single droplet studies** with **droplet ensemble, bulk and gas phase** studies to discard the spontaneous formation of urea in these phases.
- In prebiotic atmosphere of early earth, the formation of urea is an indication of CO_2 rich atmosphere along with presence of ammonia.

Background

SCIENCE ADVANCES | RESEARCH ARTICLE

CHEMISTRY

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Yifan Meng[1], Yu Xia[1,2]*, Jinheng Xu[1], Richard N. Zare[1]*

Comment

https://doi.org/10.1038/s41467-023-40351-5

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Jie Ding, Runping Ye, Yanghe Fu, Yiming He, Ye Wu, Yulong Zhang, Qin Zhong, Harold H. Kung & Maohong Fan

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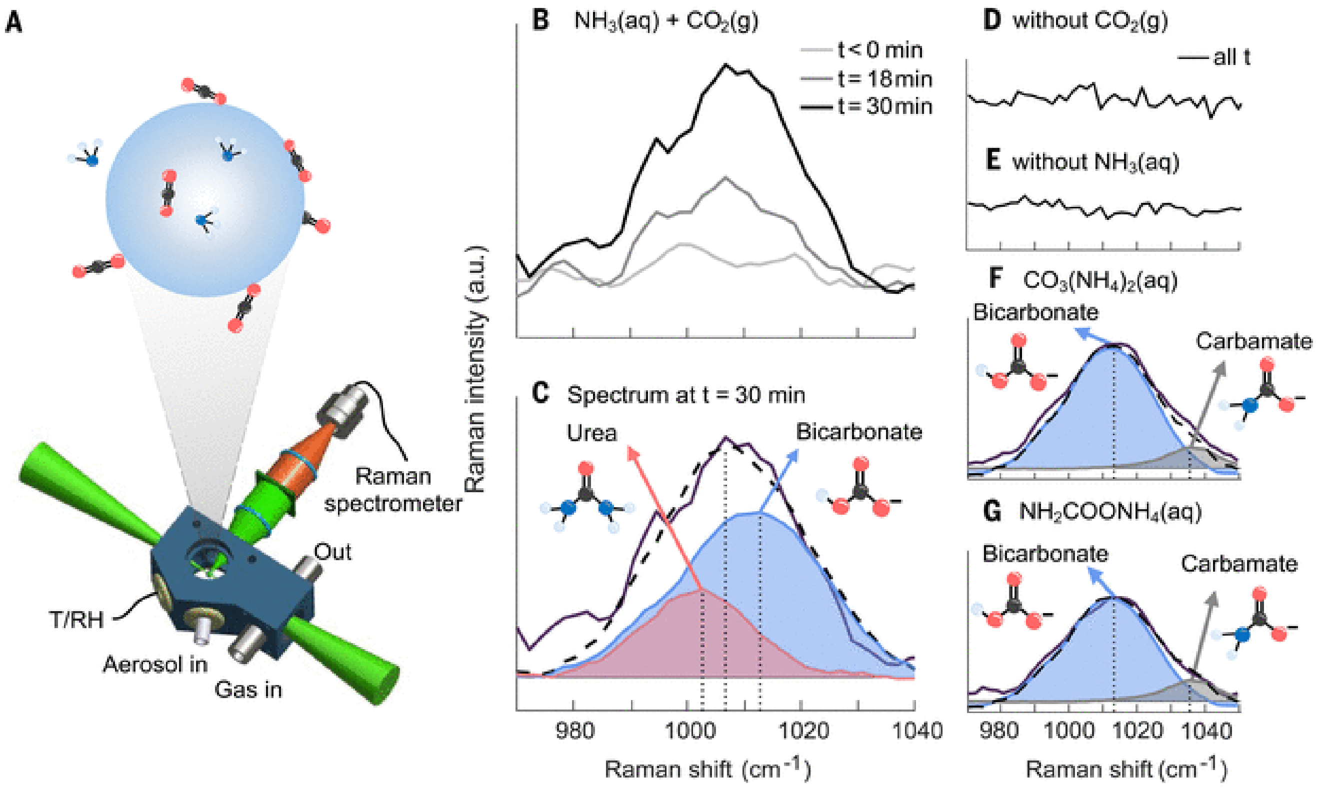
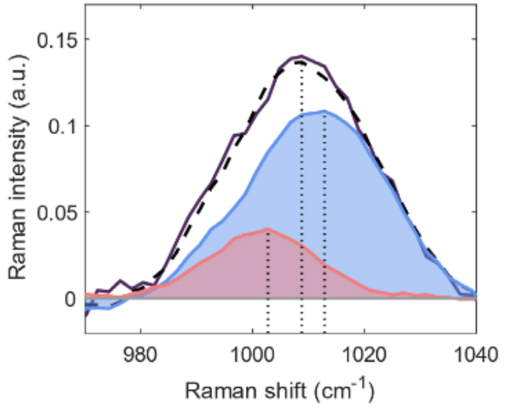
Electrocatalytic Synthesis of Urea: An In-depth Investigation from Material Modification to Mechanism Analysis

Jianghui Cao, Fang Zhao, Chengjie Li, Qidong Zhao, Liguo Gao, Tingli Ma, Hao Xu,* Xuefeng Ren,* and Anmin Liu**

Results and Discussion





With 3.5 μm droplet size

Fig. 1. Single-droplet experiments. (A) Schematic representation of a single droplet with ammonia and carbon dioxide molecules. **(B)** Single-droplet Raman spectra recorded before (t <0 min) and after (t >0 min) exposure of an aqueous ammonia [NH_3(aq)] droplet (**radius 2 μm**) to CO_2 gas [CO_2(g)]. **(C)** The decomposition of the Raman spectrum at t = 30 min shows that urea was formed in addition to bicarbonate. **(D)** Single-droplet spectrum of an NH_3(aq) droplet in nitrogen gas (N_2), i.e., without the addition of CO_2(g). **(E)** Single-droplet spectrum of a water droplet (i.e., without NH_3) in CO_2(g). No Raman bands, and thus no urea formation, was seen for **(D)** and **(E)**. **(F)** Single-droplet spectrum of a 1M ammonium carbonate droplet in CO_2(g). **(G)** Single-droplet spectrum of a 1M ammonium carbamate droplet in CO_2(g). Spectra in **(F)** and **(G)** do not show detectable amounts of urea. The droplet size was kept constant over the course of the measurement for all single-droplet experiments by adding NaCl and matching the % RH (~80%).

Results and Discussion

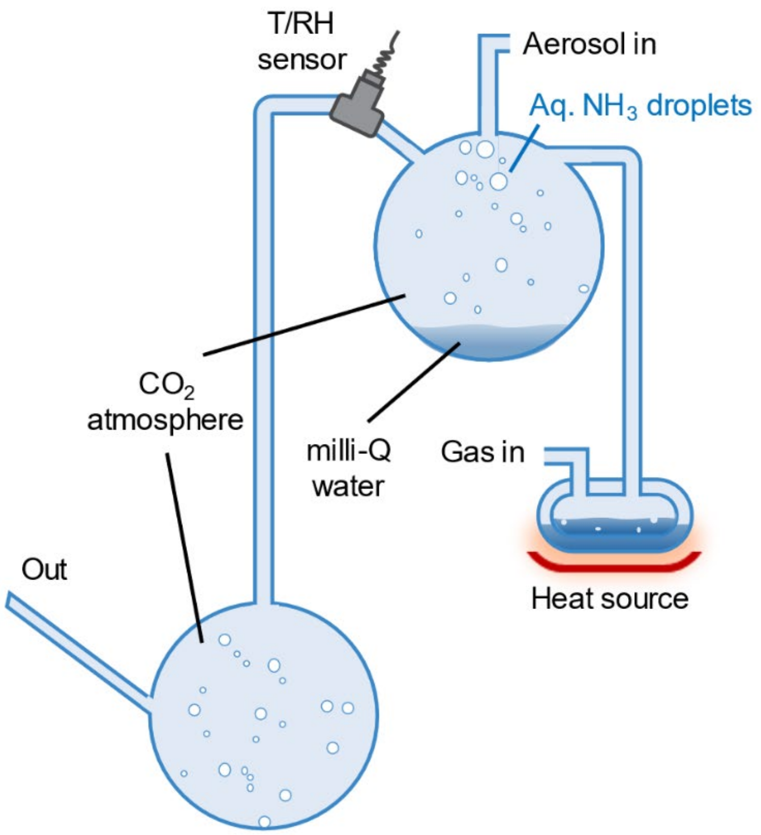


Fig. Schematic of the **droplet ensemble setup**. An ensemble of aqueous ammonia (NH_3(aq)) droplets was sprayed into two round-bottom flasks ("aerosol in") that were filled with humidified (>80% RH) CO_2 gas ("gas in") at a temperature of 20 °C. **The CO_2 gas was humidified by passing a heated (40 °C) water bubbler.** A temperature and RH (T/ RH) sensor was mounted in between the two flasks.

Results and Discussion

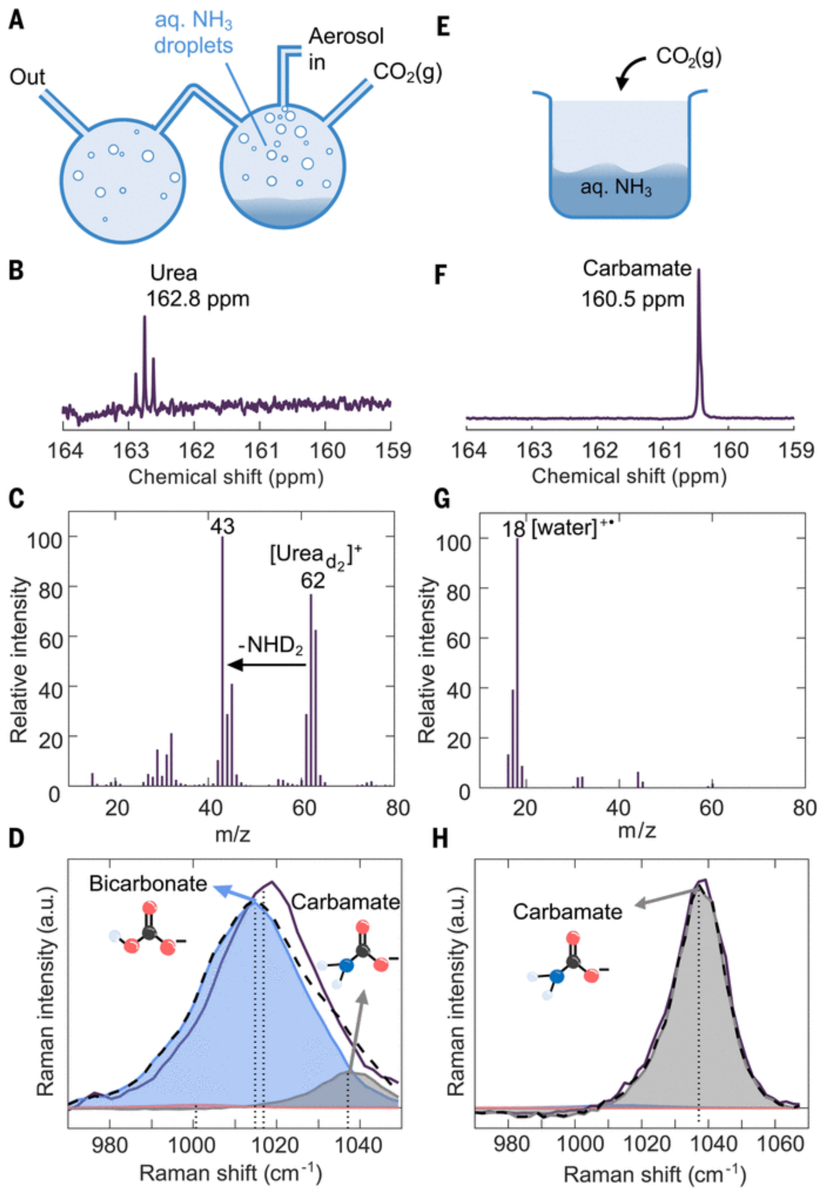


Fig. 2. Droplet ensemble and bulk experiments. (A) Schematic representation of the droplet ensemble setup. **(B)** The ^{13}C NMR spectrum of the droplet ensemble sample shows a weak urea signal at 162.8 ppm. **(C)** The mass spectrum from GC-MS of a partially deuterated droplet ensemble sample shows the characteristic patterns of partially deuterated urea (uread2, $-NHD_2$). **(D)** The Raman spectrum of the droplet ensemble sample does not show a detectable urea band, but as in Fig. 1, F and G, shows contributions from bicarbonate and carbamate. **(E)** Schematic representation of the setup for bulk studies. **(F)** The ^{13}C NMR spectrum of the bulk sample shows a carbamate signal at 160.5 ppm but no urea. **(G)** The mass spectrum from GC-MS of a partially deuterated bulk sample contains mostly water but no urea. **(H)** The Raman spectrum of the bulk sample shows only the **carbamate band but no urea.**

Results and Discussion

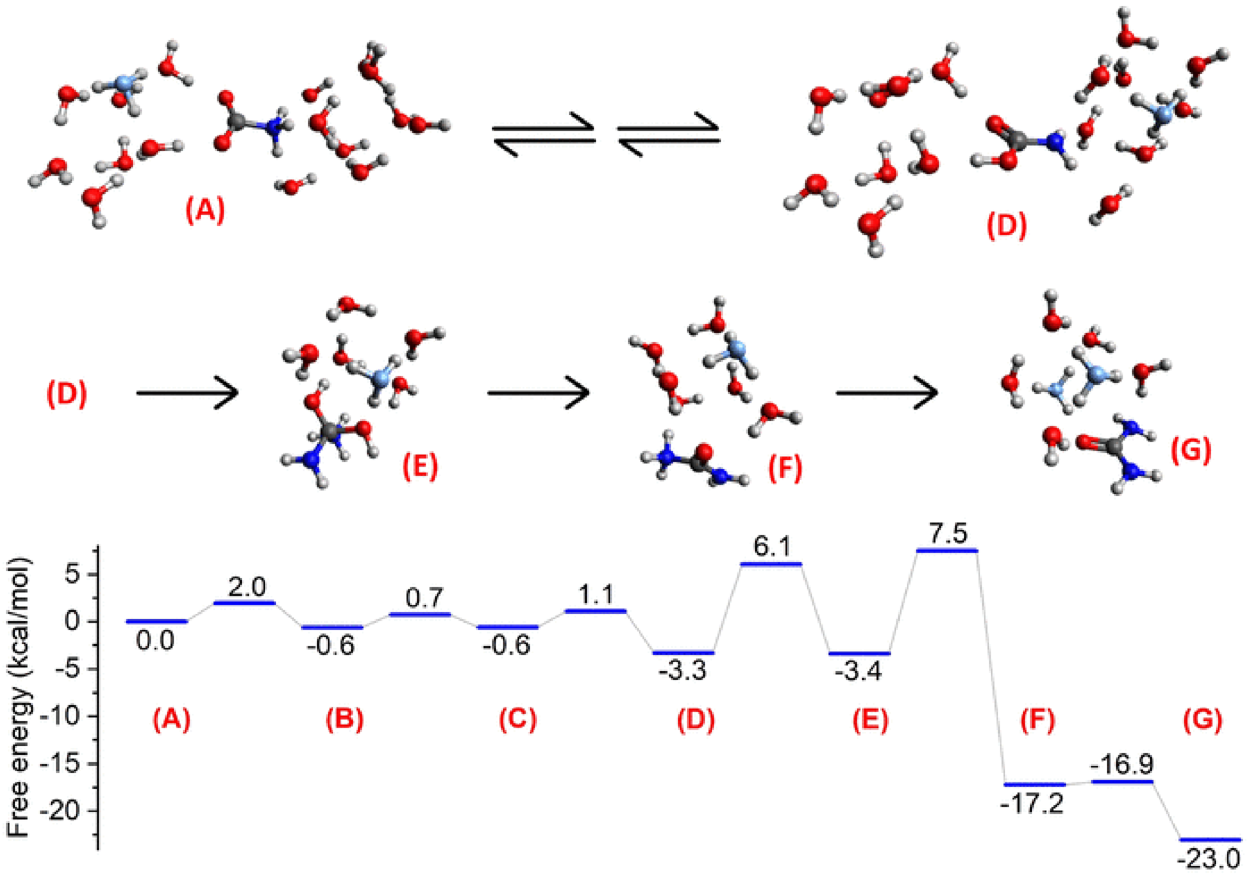


Fig. 3. Structures and free energy diagram for the formation of urea from NH_3 and CO_2. Red, blue, gray, and white balls represent O, N, C, and H atoms, respectively. Light blue indicates the O atom of hydroniums.

(Top row) Formation of carbamic acid as reactive intermediate through a number of fast reversible steps [(A) to (D)] establishing a quasi-equilibrium.

(Middle row) Rate-determining addition of the second NH_3 to carbamic acid.

(Bottom row) Free energy diagram.

Results and Discussion

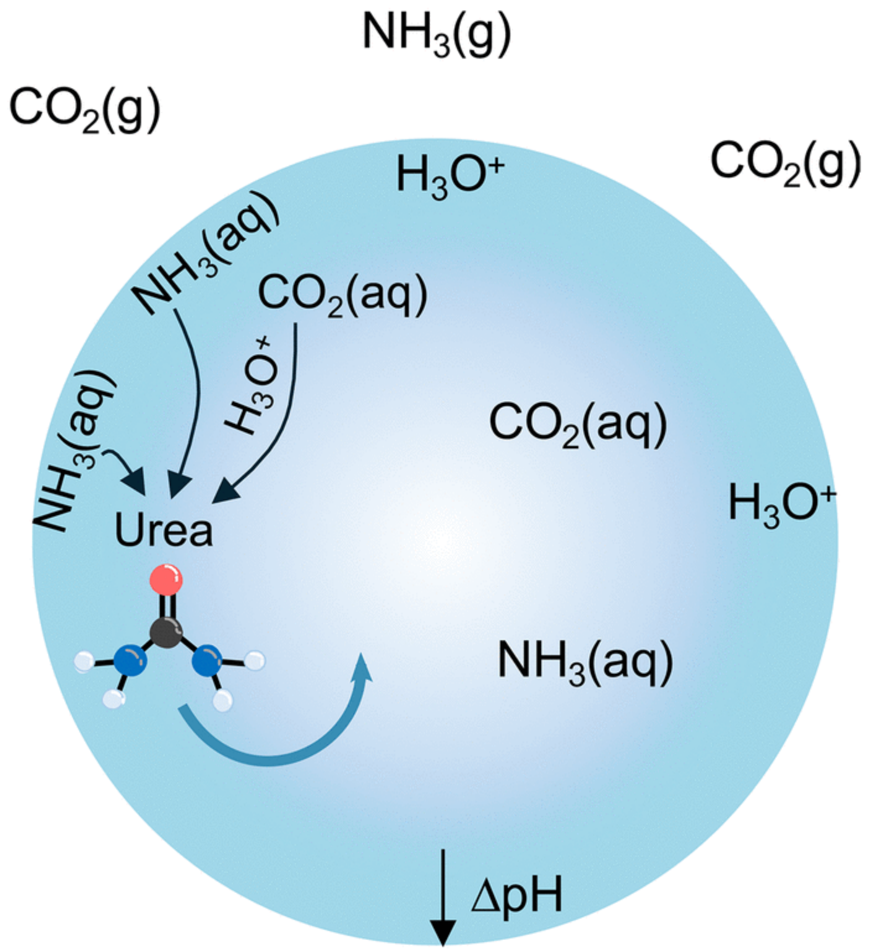
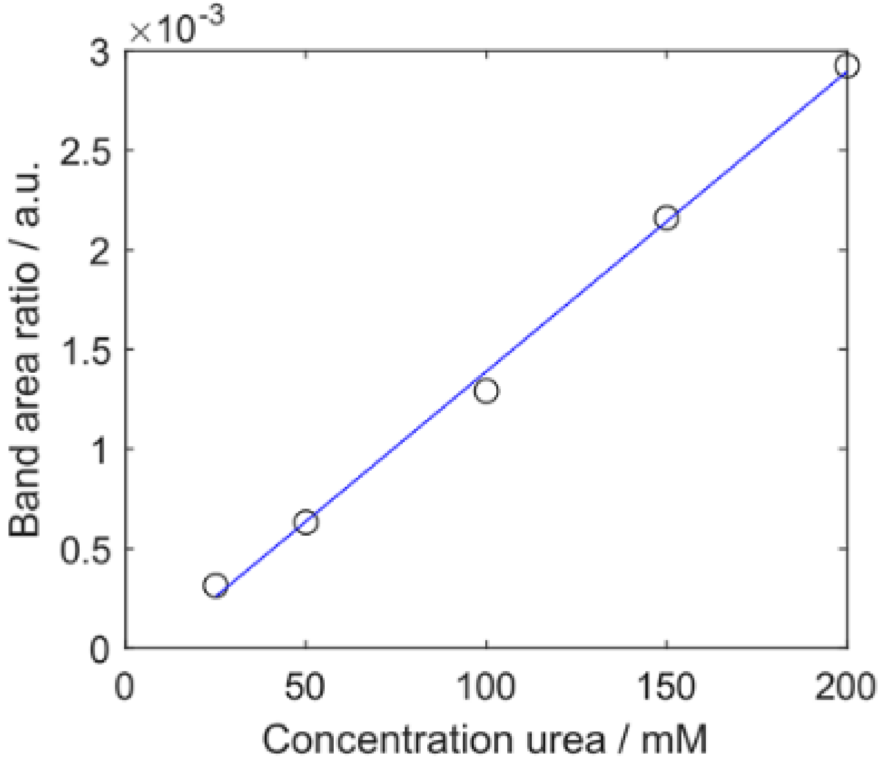


Fig. 4. Graphical representation of the **proposed mechanism** for urea formation in a droplet. Urea is formed in a multistep, proton-catalyzed reaction between partially solvated ammonia [NH_3(aq)] and carbon dioxide [CO_2(aq)] in a subsurface layer, where a pH gradient (referring H_3O^+ activity to the locally decreased reference chemical potential) creates the necessary acidic conditions.

Results and Discussion



Average formation of urea in the droplet size range of 1.5-4.0 μm (42 ± 10 mM)

Fig. Calibration curve for the determination of the urea concentration in aqueous solutions. The band area ratio corresponds to the ratio of the area under the urea Raman band to the area under the water stretching band.

Results and Discussion

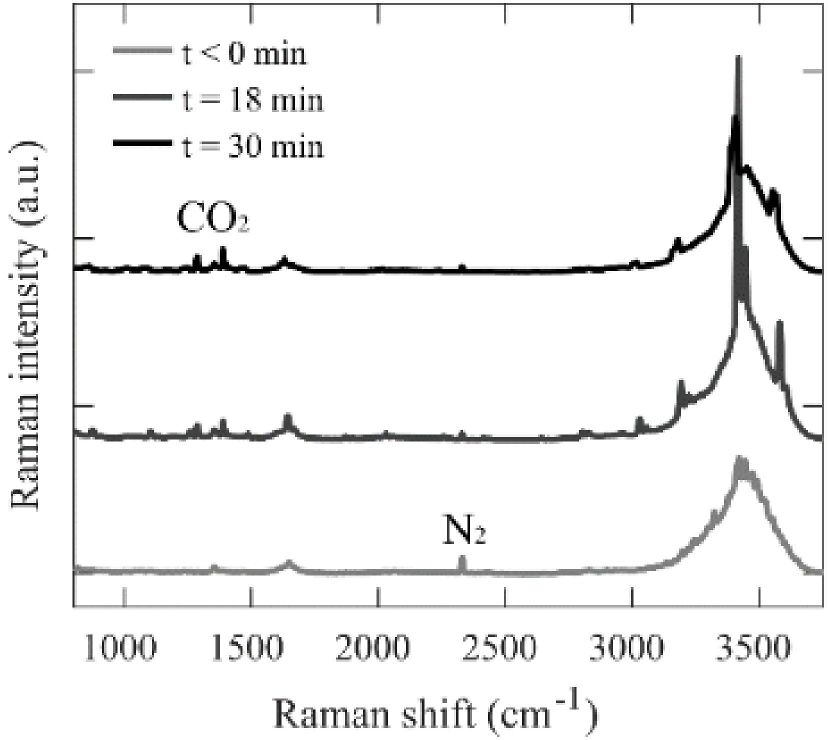


Fig. Overview Raman spectra during urea formation recorded at different times before ($t < 0$) and after ($t > 0$) exposure to CO_2 gas. At $t < 0$, the droplet was exposed to pure N_2 gas. At $t > 0$, the droplet was exposed to a CO_2/ N_2 gas mixture with a gas ratio of 3 (**75 % CO_2 and 25 % N_2**) at a total pressure of **1bar**.

Results and Discussion

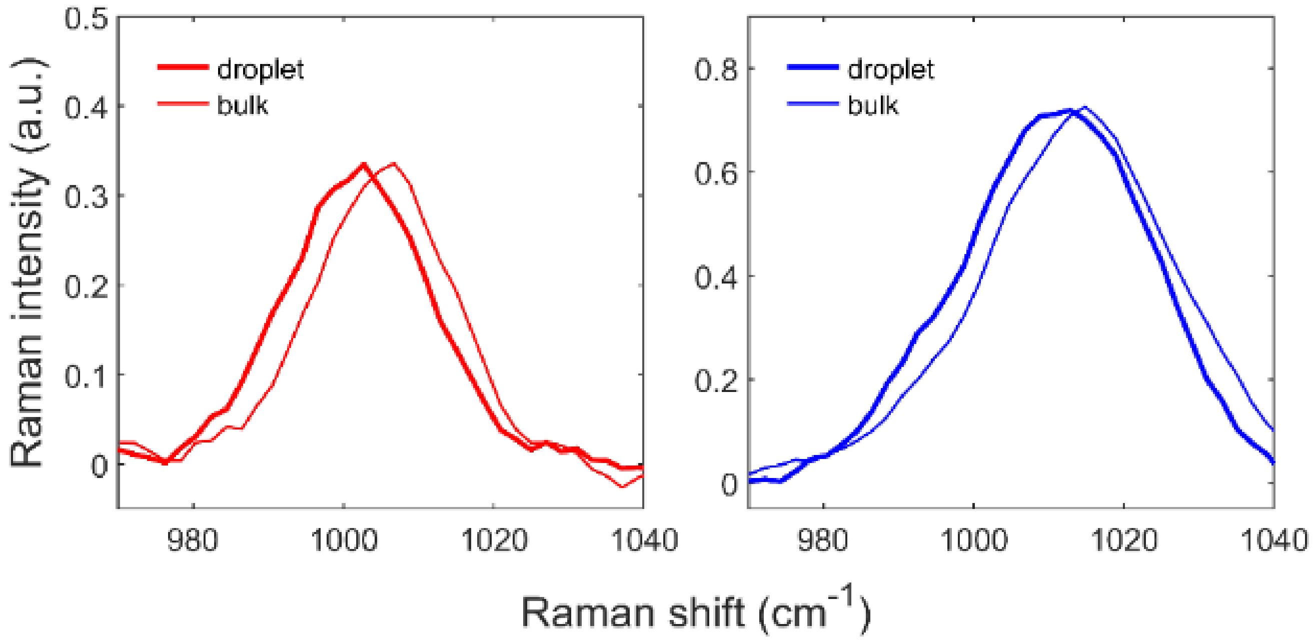


Fig. Left: Raman reference spectra of aqueous urea solutions obtained from single trapped droplets **(thick red line)** and from bulk solutions (thin red line). Right: Raman reference spectra of aqueous bicarbonate solutions obtained from single trapped droplets **(thick blue line)** and from bulk solutions (thin blue line).

Results and Discussion

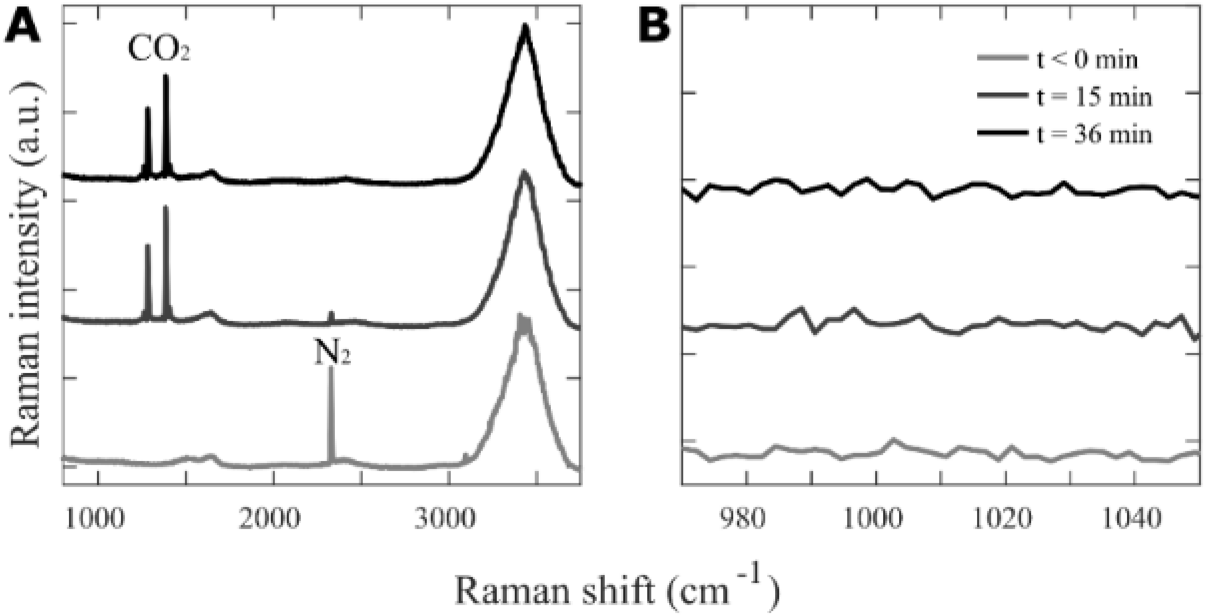


Fig. Time-dependent Raman spectra **without NH_3** (A) Overview spectra. The N_2 ($t < 0$) and the CO_2 ($t > 0$ min) pressures were 1bar. Note that **hardly any WGMs are visible in this spectrum because of the small droplet size.** (B) The same expanded region as shown in Fig. 1E. The time-dependent spectra show no urea band.

Conclusions

- ✓ **Urea formation in single droplet:** Urea spontaneously forms from CO_2 and NH_3 in aqueous droplets under ambient conditions, a novel pathway not observed in bulk liquid reactions.
- ✓ **Interfacial microreactor mechanism:** The droplet surface acts as a "**microscopic flow reactor**" with pronounced chemical gradients, enabling an unconventional proton-catalyzed reaction via **neutral carbamic acid** as the key intermediate
- ✓ **Experimental & Computational validation:** Urea formation was directly confirmed in single, optically trapped droplets **(42 ± 10 mM)** via **Raman spectroscopy, supported by ensemble GC-MS/ ^{13}C NMR**, and corroborated by quantum chemical calculations and a reaction-diffusion model consistent with experimental findings.
- ✓ **Prebiotic & broad droplet chemistry implications:** This work suggests a nonenergetic abiotic route for urea synthesis relevant to prebiotic Earth conditions, establishing a general mechanistic scheme for distinctive droplet chemistry driven by high surface-to-volume ratios and interfacial gradients