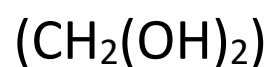


Supporting Information

Rapid preparation of gaseous methanediol



*Yi-Fang Chen and Li-Kang Chu**

Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Rd., Hsinchu
300044, Taiwan.

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1. Experimental sections

1.1. Chemicals

Paraformaldehyde was purchased from Alfa Aesar (97 %) for use without further purification. Deionized water at a resistivity of 18.2 M Ω -cm was obtained from a water purification system (SIMS00001, Merck Millipore).

1.2. Sample preparations

1.2.1. Formaldehyde solution

The 10 % (w/w) formaldehyde solution was prepared upon dissolving 6.006 g of paraformaldehyde in 54.01 g of water, followed by the reflux at 85 °C for 300 minutes. Then the solution was filtered with a syringe filter (pore size: 0.22 μ m; diameter: 33 mm, PVDF, All Line Technology). The solution was bathed in *ca.* 32 °C and the vapour was continuously injected to the gas chamber and exhausted to reach the stationary condition. The length and diameter of the cylindrical stainless-steel chamber were 15.0 and 3.7 cm, respectively, and the ends were sealed with two BaF₂ windows (diameter = 25.0 mm, thickness = 3.0 mm, Model No. 87-701, Edmund Optics) to allow the detection region of > 833 cm⁻¹. The pressure was read by two capacitance gauges (626C12TBE, 626C11TQE, MKS U.S.A).

1.2.2. CH₂O vapour

The vapour of CH₂O was prepared via the pyrolysis of paraformaldehyde at *ca.* 50 °C. By tuning the pumping capacity, the pressure of CH₂O was adjusted and the infrared spectra were acquired concomitantly, as shown in **Fig. S1**. The calibration of the integrated infrared absorbances at 2682.4 – 2927.5 cm⁻¹ with respect to the pressures of the pure CH₂O was also derived, as shown in **Fig. S2**.

1.2.3. H₂O vapour

The vapour of H₂O was prepared by evaporating liquid H₂O in a water bath at *ca.* 35 °C. By tuning the pumping capacity, the pressure of H₂O was adjusted and the infrared spectrum was acquired

concomitantly. It was used for comparison with the spectrum of the vapour of the formaldehyde solution described in **Section 1.2.1**, as shown in **Fig. S3**. The partial pressure of H₂O in the vapour from the formaldehyde solution was approximated as 14.3 Torr.

1.3 Steady-state Fourier-transform infrared spectroscopy

The gas chamber was mounted in the absorption compartment of a Fourier-transform infrared spectrometer (Vertex 80, Bruker) operating in continuous-scan mode to collect the infrared absorption spectra of the aforementioned samples in 0–8000 cm⁻¹ at a spectral resolution of *ca.* 0.4 cm⁻¹. Each spectrum was acquired upon averaging 128 scans for a better signal-to-noise ratio.

2. Spectral simulation

The rovibrational contours of the symmetric (ν_s) and antisymmetric (ν_{as}) O–C–O stretching modes of CH₂(OH)₂ were simulated using the PGOPHER program.²⁴ The predicted rotational parameters in the vibrational ground and excited states, predicted with the density functional theory B3LYP with the basis set aug-cc-pVTZ for these two vibrational modes, were adapted from Table S12 of Ref. 22. The temperature was set at 298 K and the maximum J quantum number was 100. A linewidth of 0.52 cm⁻¹ using the Gaussian function was used for constructing the simulated spectrum. Since the predicted infrared intensity is presumably not quantitatively precise, the predicted relative intensity of $I(\nu_s)/I(\nu_{as})$ of 0.32 was adjusted to 0.54 to better fit the observation, just as previously reported.²²

3. Supplementary figures

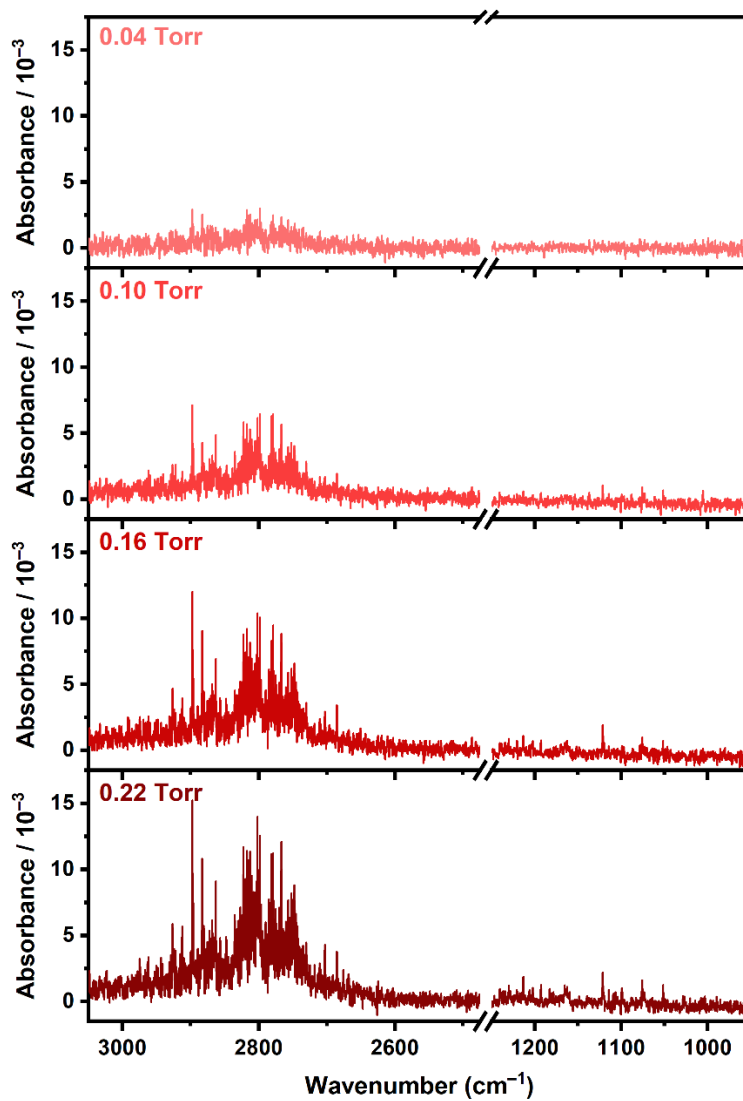


Fig. S1 Absorption spectra of CH₂O at different pressures.

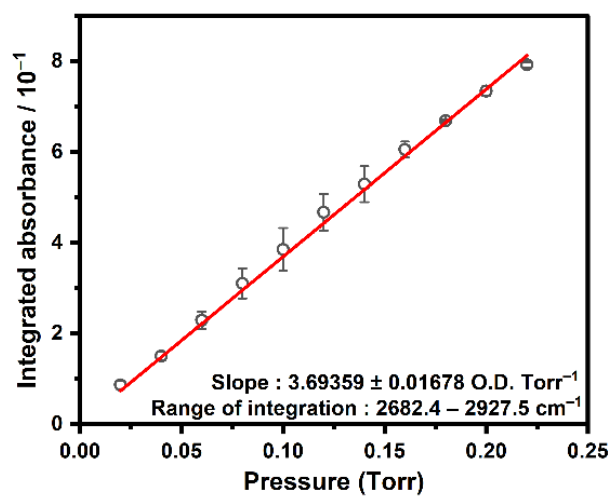


Fig. S2 The calibrations of the pressures and the integrated absorbances of CH₂O.

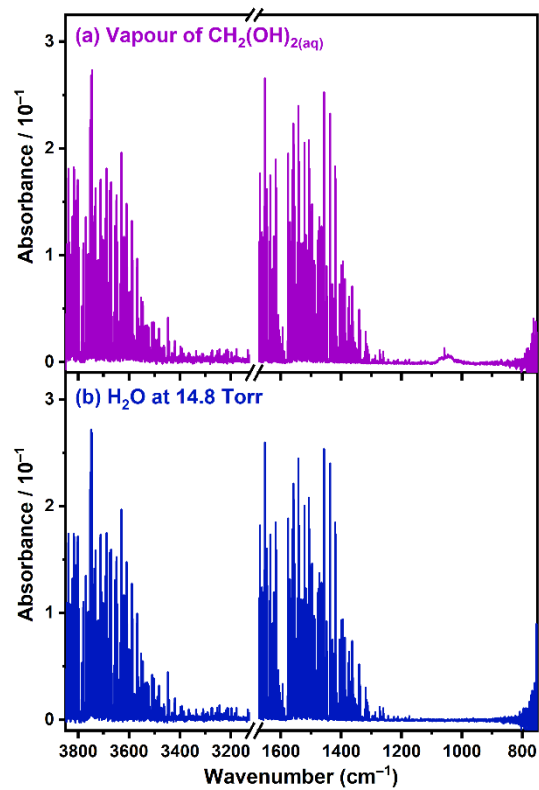


Fig. S3 Comparison of the observed infrared spectra of (a) vapour of formaldehyde solution (**Fig. 1a**) and (b) pure H_2O pressure at 14.8 Torr.