Supplemental Material

Two-Dimensional Correlation Spectroscopy (2D-COS) of Gas-Phase Pyrrole **Clusters in a Supersonic Jet: Treatment of Sharp Bands on a Broad Background**

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(b)





Fig. S1 A treatment of the spline interpolation in "Origin", which is a computer program for scientific graphing and data analysis (https://www.originlab.com/).
(a) Putting anchor points on the observed IR spectrum. We first obtain a linear interpolation of zig-zag type before a spline treatment. (b) Spline curves are interpolated between anchor points. A baseline with red line is slightly deviated from the observed broad background. Only 8 anchor points on the spectrum is insufficient to perform a

better extraction of broad background. (c) Spline curves are fitted to the observed broad background by adding anchor points and moving the position of each anchor point. If we use 15 anchor points and move their positions properly, the well-fitted broad background can be obtained. Subtraction of the background from the observed IR spectrum, we can extract only the sharp bands in the IR spectrum, as shown in Fig. 3(a).



Fig. S2 (a) Broad components extracted from the experimental IR spectra shown in Fig. 1(c). A decomposition treatment is done by using a method of the spline extrapolation, which is explained in Fig. S1. (b) Asynchronous 2D correlation IR spectrum, which is obtained



from the decomposed broad spectra shown in (a).

Fig. S3 Intensities of three sharp bands and two broad bands to draw the simulated IR spectra shown in Figs. 4(a) and 4(b), respectively. A perturbation value on a horizontal axis corresponds to the temperature of the Py liquid sample in our experiment.



Fig. S4 Enlarged simulated asynchronous 2D correlation spectra of Figs. 5(a) ~ 5(c), respectively.