Electronic Supplementary Material

Title: Mechanism of hexamethylenetetramine (HMT) formation in interstellar conditions

Authors: V. Vinogradoff,*† A. Rimola,*‡ F. Duvernay,† G. Danger,† P. Theulé,† and T. Chiavassa†

†Laboratoire de Physique des Interactions Ioniques et Moléculaires, Centre St-Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille, France.
‡Departament de Química, 08193, Bellaterra, Spain.

E-mail corresponding authors: vass_vino@yahoo.fr, albert.rimola@uab.cat

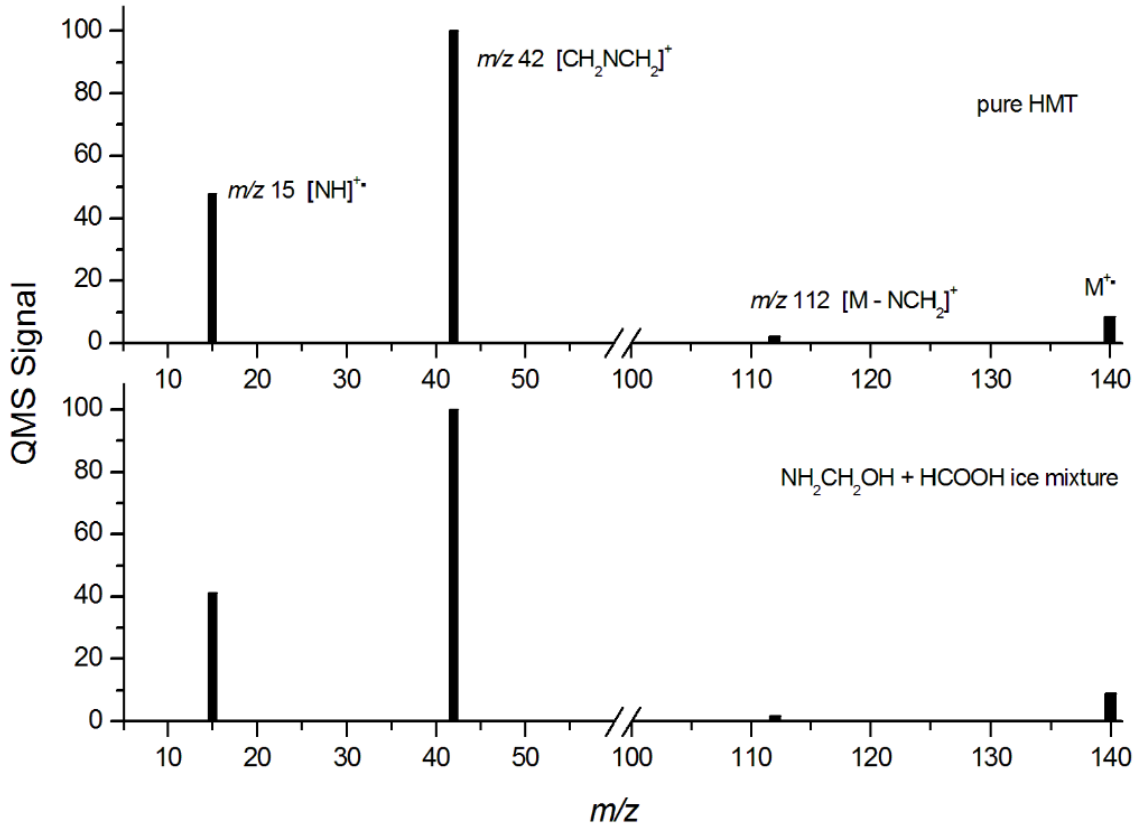

Figure S1. QMS signal recorded for pure HMT at 260 K (top panel) and from the warming of NH_2CH_2OH : HCOOH ice mixture at 360 K (bottom panel).

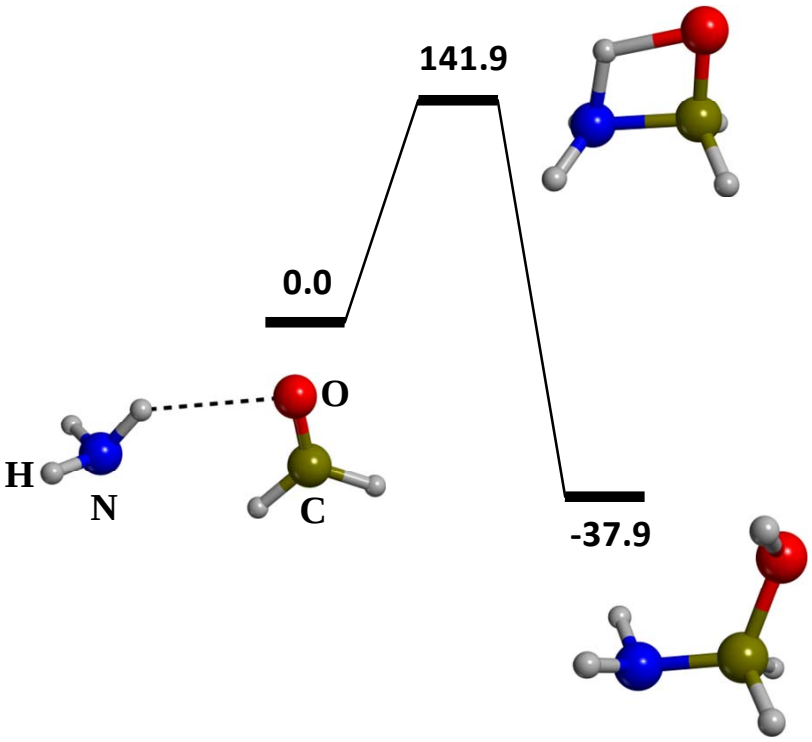

Figure S2. B3LYP/6-311++G(d,p) potential energy profile for the gas phase formation of aminomethanol adopting the reaction of NH_3 + $H_2C=O$ → NH_2CH_2OH. Units in kJ mol^{-1}.

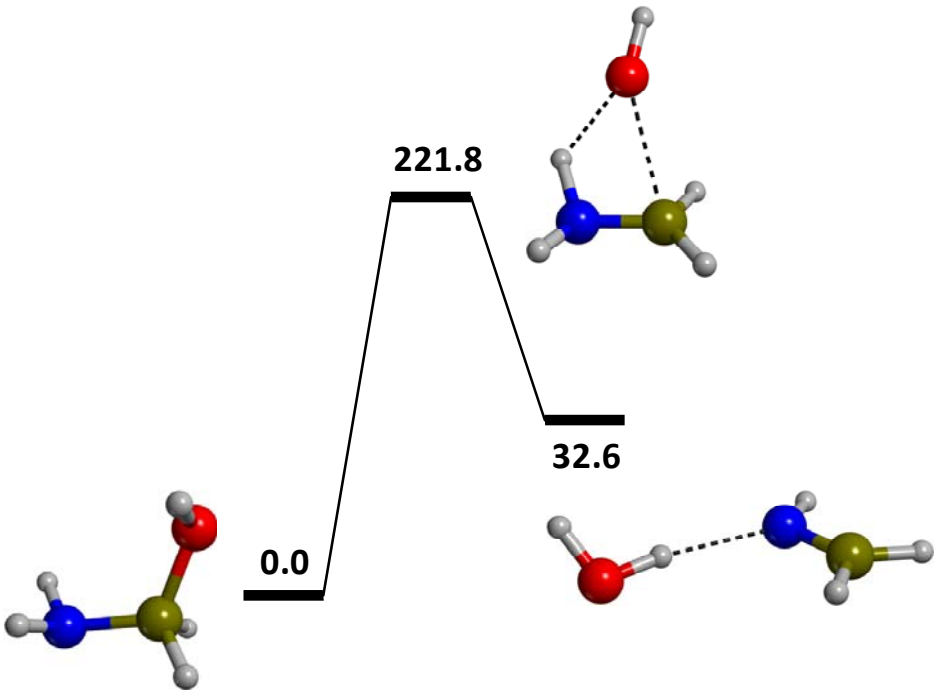

Figure S3. B3LYP potential energy profile for the gas-phase dehydration of aminomethanol to give methylenimine adopting the reaction of $NH_2CH_2OH \rightarrow CH_2NH + H_2O$. Units in kJ mol^{-1}.

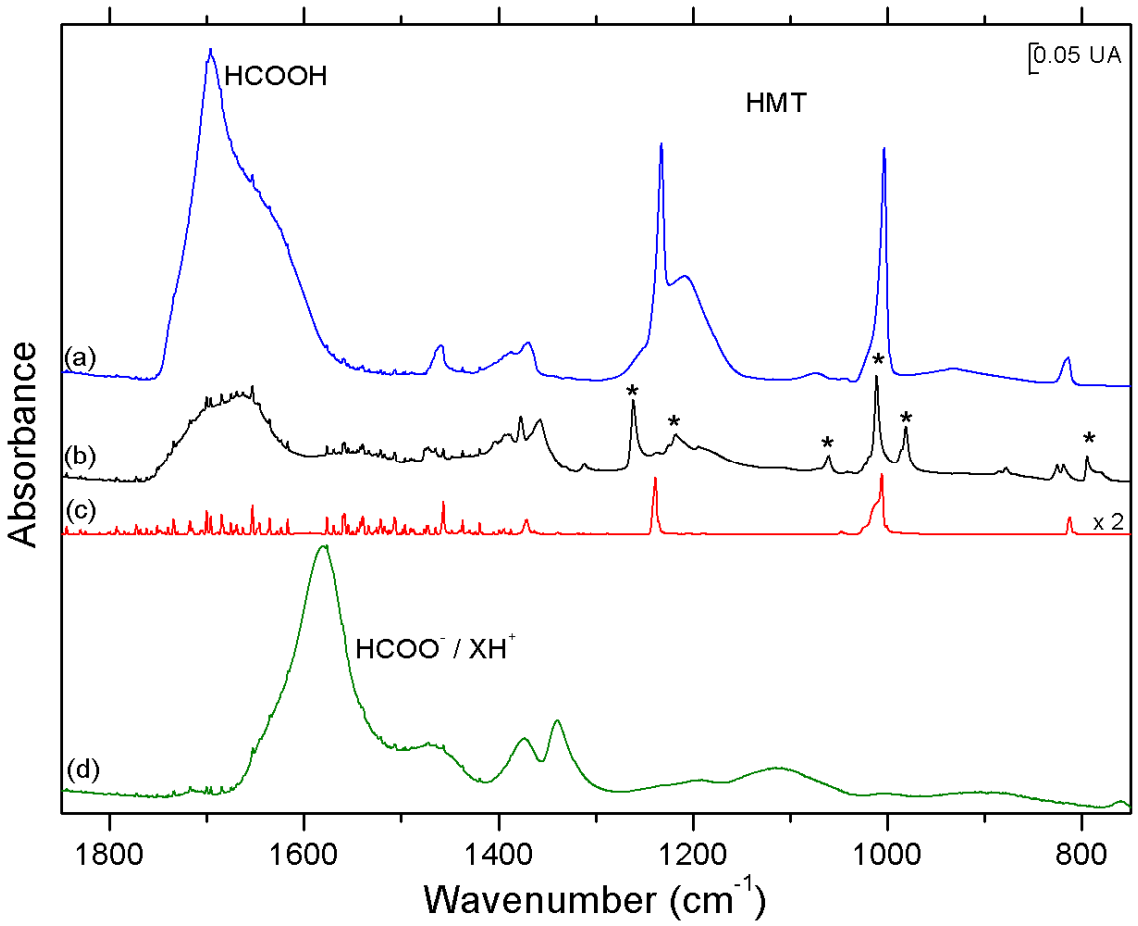

Figure S4. Infra-Red spectra of a HMT:HCOOH ice mixture at 100 K (a), 240 K (b), 250 K (c), and comparison with the $HCOO^-$ XH^+ salt species at 250 K (d).

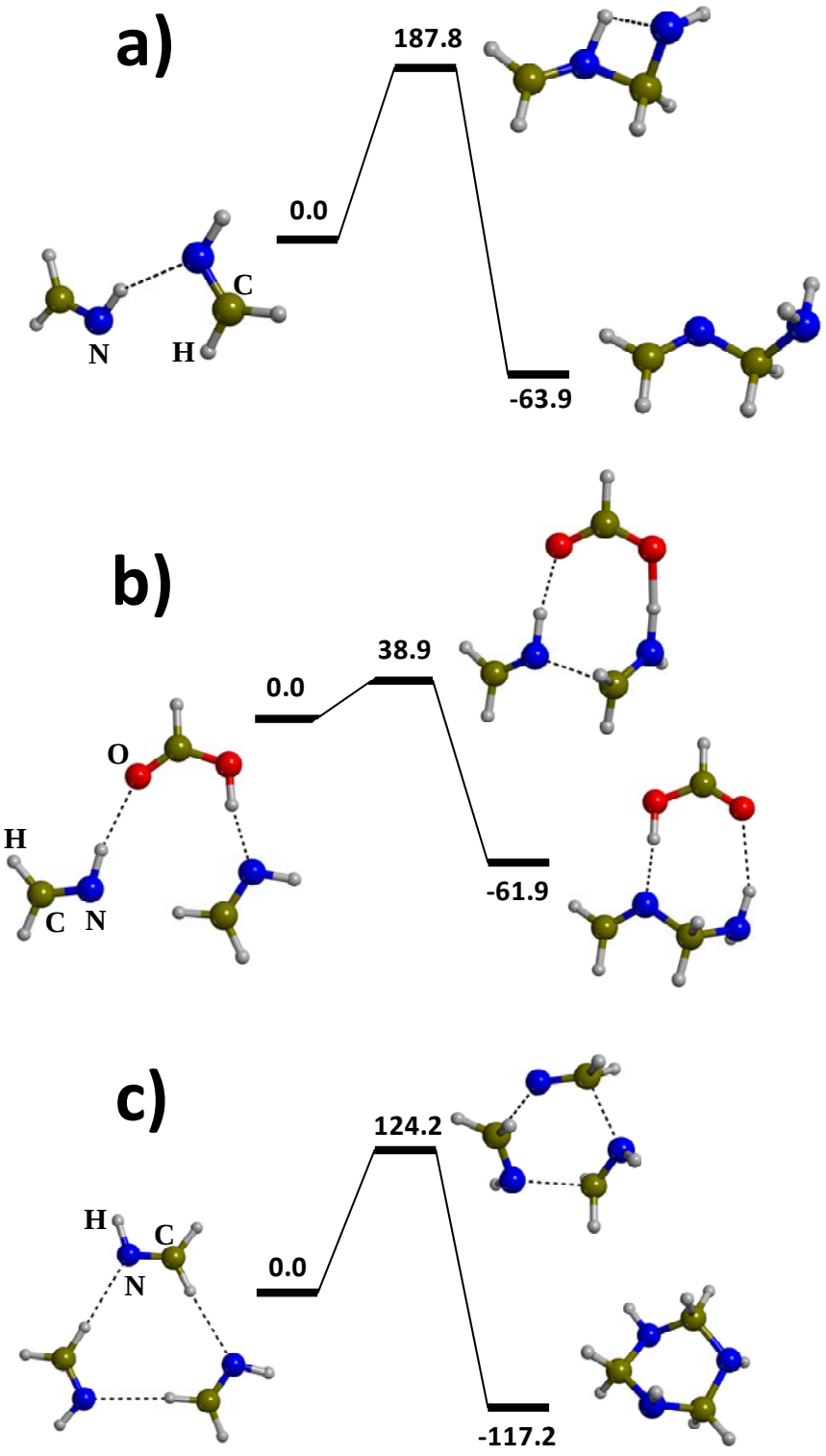

Figure S5. B3LYP-potential energy profiles for the reaction between two CH_2NH molecules to form $CH_2NCH_2NH_2$ in gas phase (a) and in the presence of HCOOH (b). Formation of trimethylentriamine from condensation of three CH_2NH molecules (c). Units in kJ mol^{-1}.

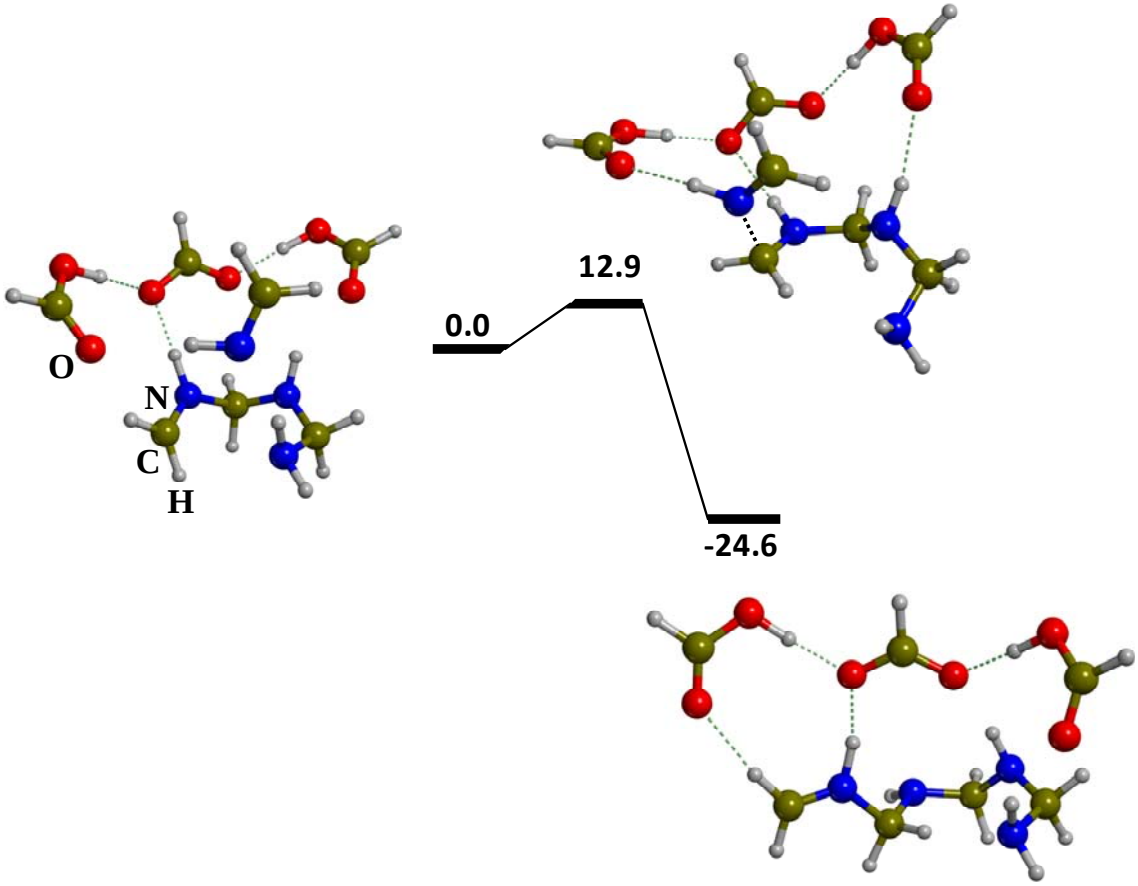

Figure S6. B3LYP-potential energy profile relative to the addition of CH_2NH on $NH_2CH_2NHCH_2NHCH_2^+$, as a further step for the elongation of polymethylenimine (PMI). Units in kJ mol^{-1}.

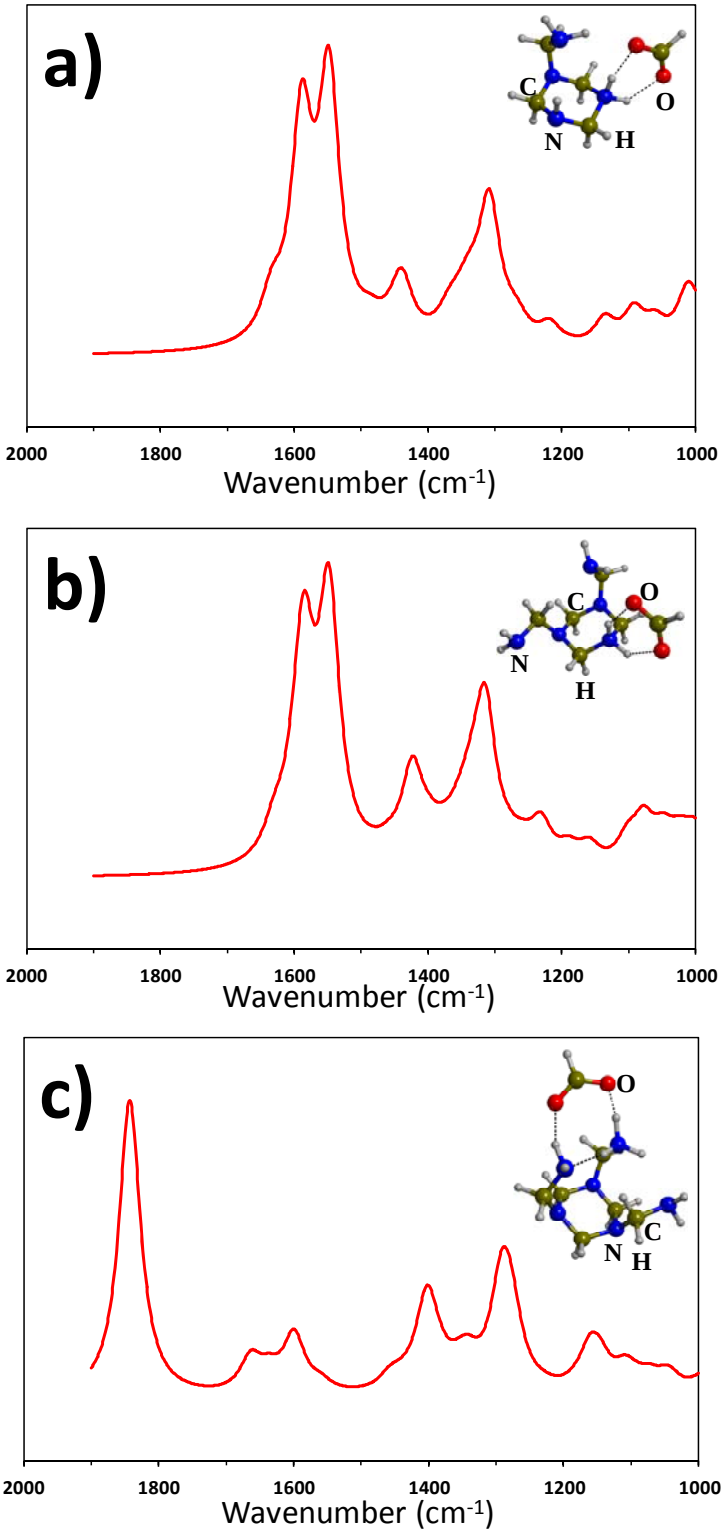

Figure S7. B3LYP-simulated IR spectra of possible candidates to be the $HCOO^-$ XH^+ salt observed experimentally: a), b) and c) refers to $TMTH^+$ upon addition of one, two and three CH_2NH molecules, respectively.

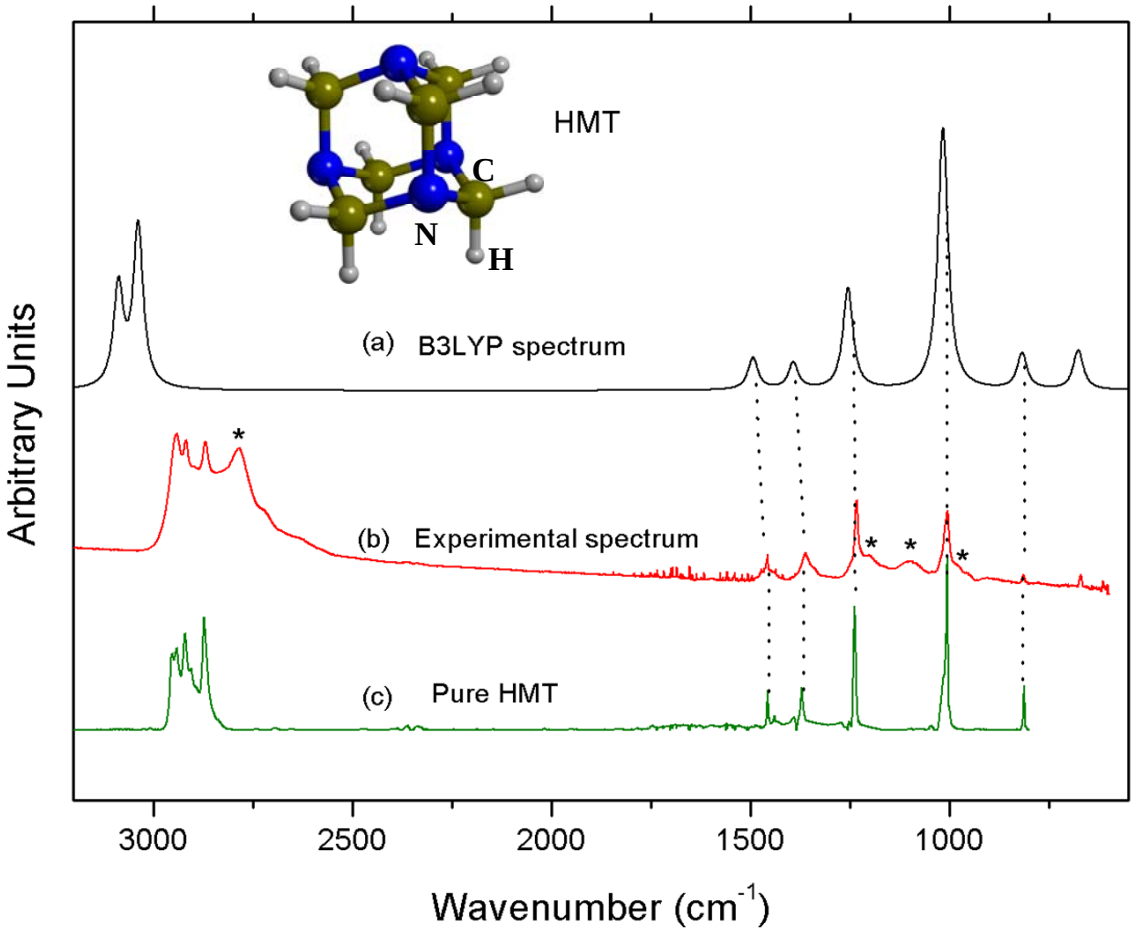

Figure S8. Comparison between the IR spectra of HMT simulated at B3LYP (a), the experimental spectrum of HMT formed at 330 K from a CH_2NH:HCOOH ice mixture (stars are assigned to PMI) (b), and pure HMT at 250 K (c).