Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information:

Vibrational Spectroscopy of $Cu^+(H_2)_4$: About Anharmonicity and Fluxionality

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Table S1 Optimized coordinates for $Cu^+(H_2)_4$ structures at CCSD(T)/def2-TZVPP (in parentheses: MP2/def2-TZVPP) level. The structures and their simulated spectra are shown in Fig. S1. The interatomic distances are given in pm. The interatomic distances – especially for the near H_2 – are notably shorter at the MP2 level than at the CCSD(T) level.

$C_s(1)$	r(Cu–H_2)	r(H–H)	φ(H_2–Cu–$H_2^{(far)}$)	φ(H_2–Cu–$H_2^{(near)}$)
far H_2	183.3 (180.0)	76.6 (76.5)	–	–
unique near H_2	175.2 (167.6)	77.4 (77.9)	108.3 ° (107.1 °)	112.5 ° (113.6 °)
pair of near H_2	176.9 (169.2)	77.2 (77.7)	105.7 ° (104.4 °)	111.5 ° (112.8 °)

$C_s(0)$	r(Cu–H_2)	r(H–H)	φ(H_2–Cu–$H_2^{(far)}$)	φ(H_2–Cu–$H_2^{(near)}$)
far H_2	182.6 (180.0)	76.7 (76.5)	–	–
unique near H_2	176.9 (169.7)	77.2 (77.6)	105.4 ° (103.5 °)	112.1 ° (113.1 °)
pair of near H_2	176.4 (168.1)	77.3 (77.8)	107.4 ° (106.2 °)	111.9 ° (113.8 °)

C_{2v}	r(Cu–H_2)	r(H–H)	φ(H_2–Cu–$H_2^{(equiv)}$)	φ(H_2–Cu–$H_2^{(other)}$)
pair of in-σ-plane H_2	175.3	77.4	113.7 °	109.6 °
pair of out-of-σ-plane H_2	180.8	76.8	104.3 °	

$D_{2d}(4)$	r(Cu–H_2)	r(H–H)	$\varphi^{(i-p)}$(H_2–Cu–H_2)	$\varphi^{(o-o-p)}$(H_2–Cu–H_2)
quadruple of H_2	178.1	77.1	110.1 °	109.2 °

$D_{2d}(0)$	r(Cu–H_2)	r(H–H)	$\varphi^{(i-p)}$(H_2–Cu–H_2)	$\varphi^{(o-o-p)}$(H_2–Cu–H_2)
quadruple of H_2	178.1	77.1	108.1 °	110.2 °

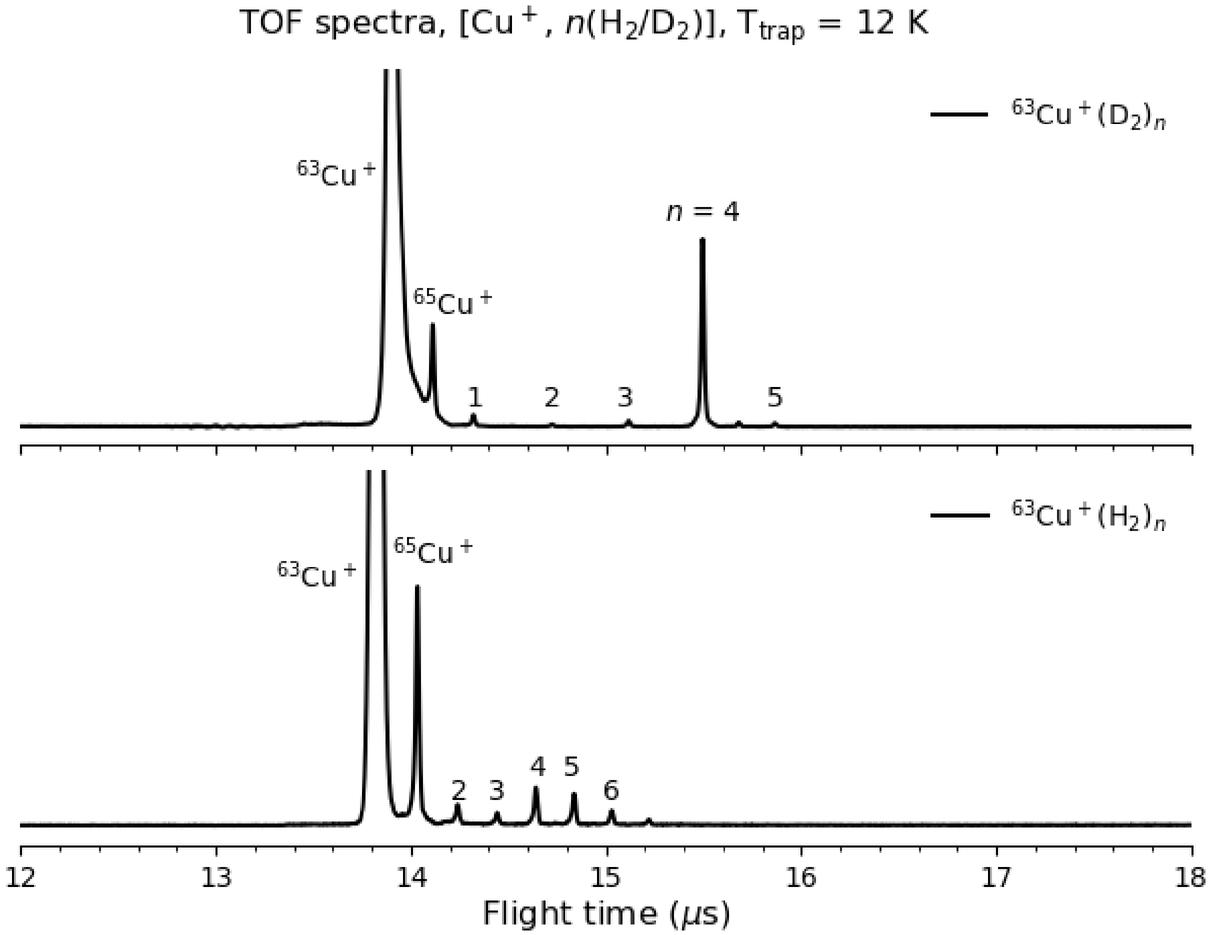


Fig. S1 Time-of-flight (TOF) spectra obtained after trapping and accumulating mass-selected $^{63}Cu^+$ cations for 99 ms in pure H_2/D_2 at 12 K.

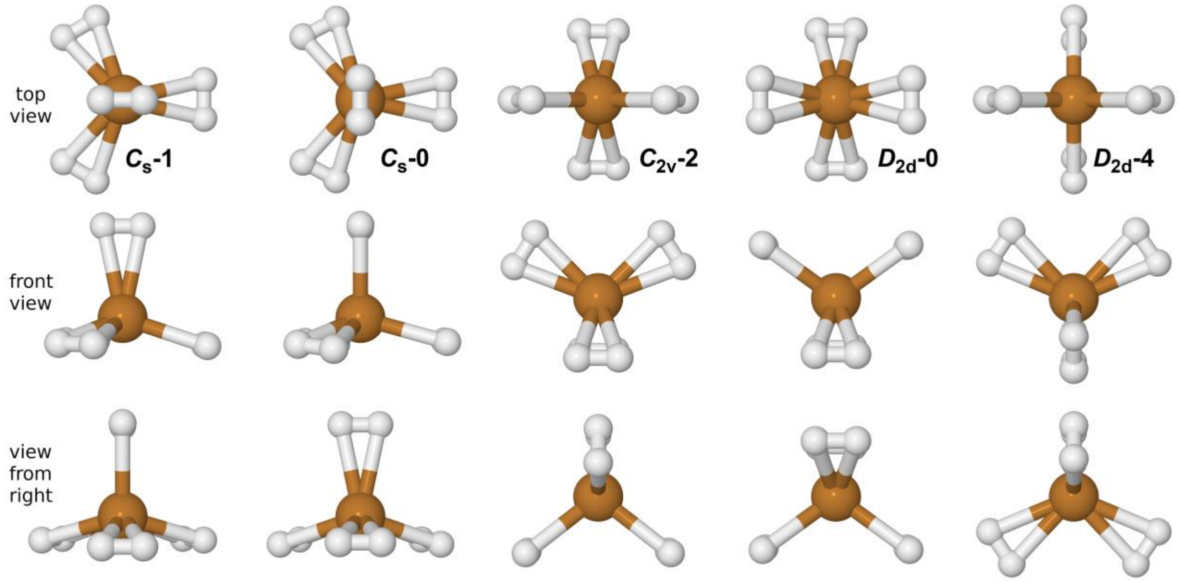


Fig. S2 High-symmetry structures of $Cu^+(H_2)_4$ in tetrahedral coordination with views from different angles.

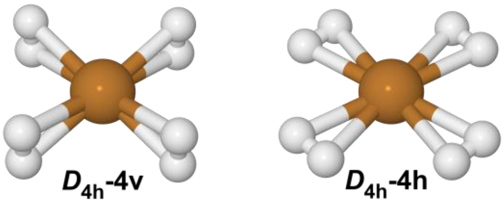
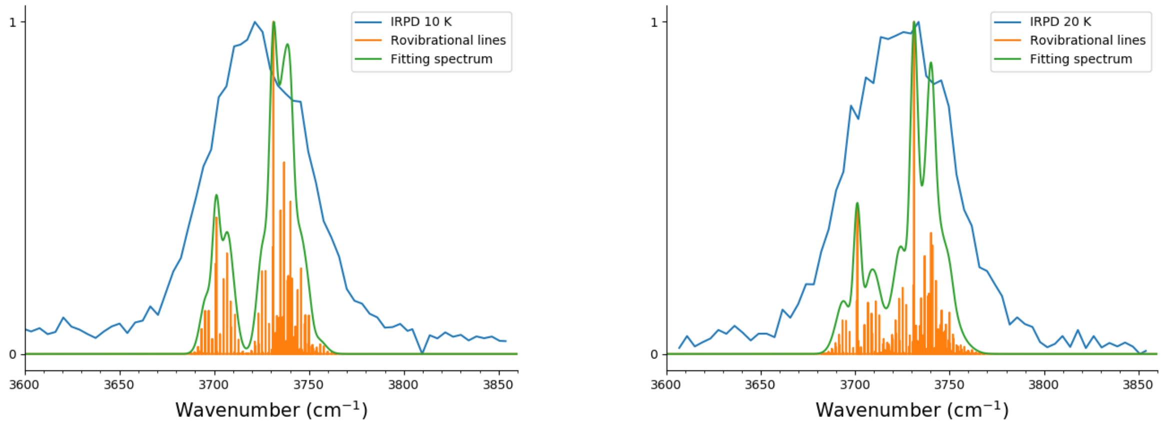
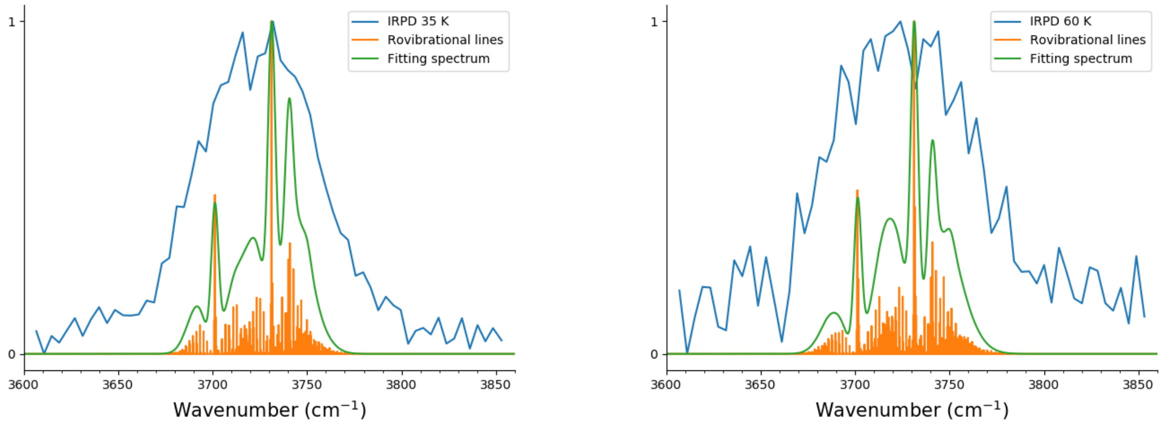


Fig. S3 High-symmetry structures of $Cu^+(H_2)_4$ with square planar coordination.



(a) T_{trap} = 10 K (b) T_{trap} = 20 K



(c) T_{trap} = 35 K (d) T_{trap} = 60 K

Fig. S4 IPRD spectra and simulated rovibrational profiles of $Cu^+(H_2)_4$ at different temperatures. The IRPD spectra are measured at different trap temperatures, (a) 10 K, (b) 20 K, (c) 35 K, and (d) 60 K. The rovibrational lines are simulated at different temperatures using PGopher (10.1). The rotational constants and quartic centrifugal distortion constants for vibrational ground state and excited states of the minimum-energy structure are calculated from DVPT2 anharmonic vibrational simulation at MP2/def2-TZVPP level. The linewidth for simulation is assumed as 4.5 cm^{-1}, considering the laser linewidth of 3.5 cm^{-1} and assuming 1 cm^{-1} broadening from predissociation lifetime.

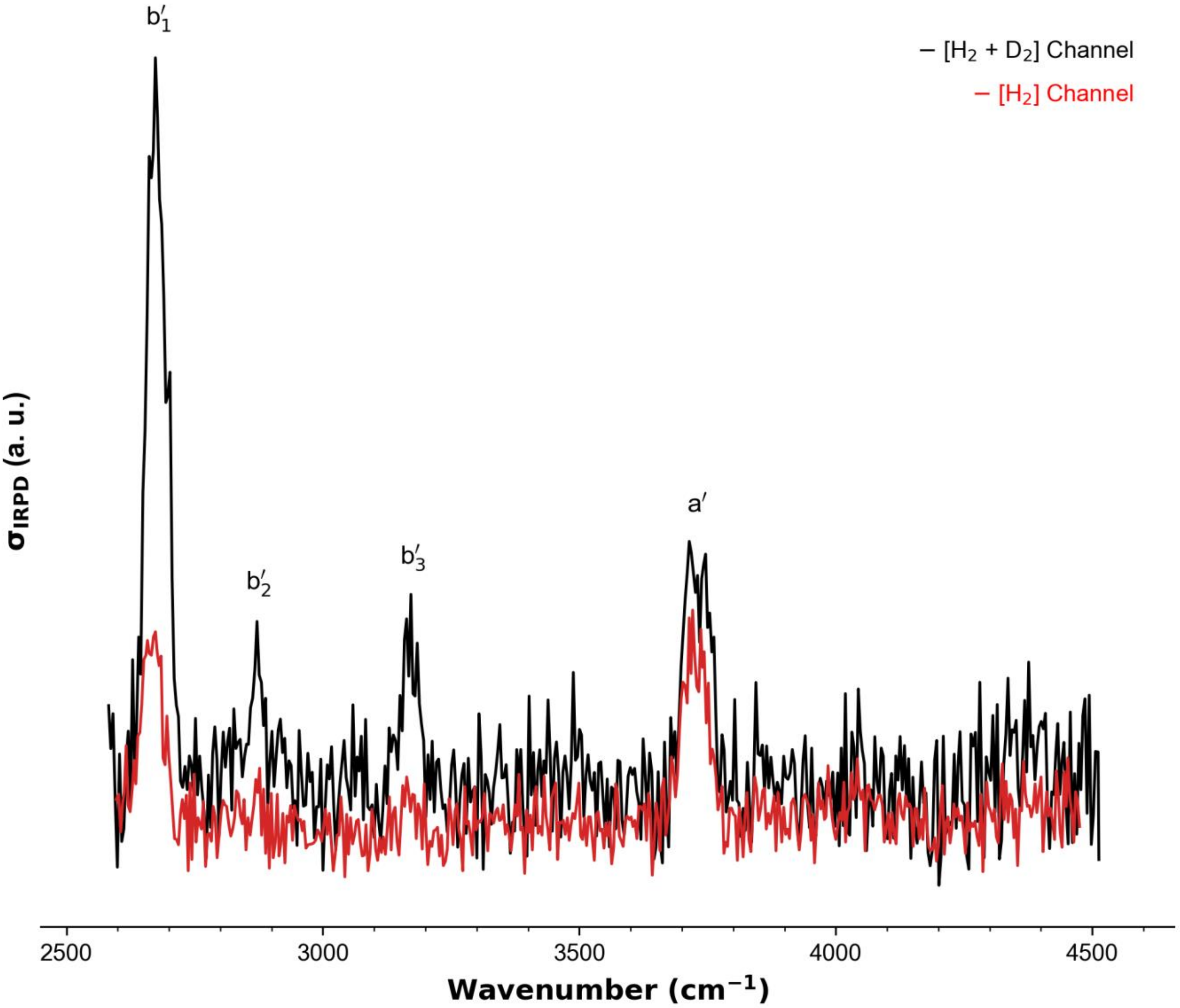
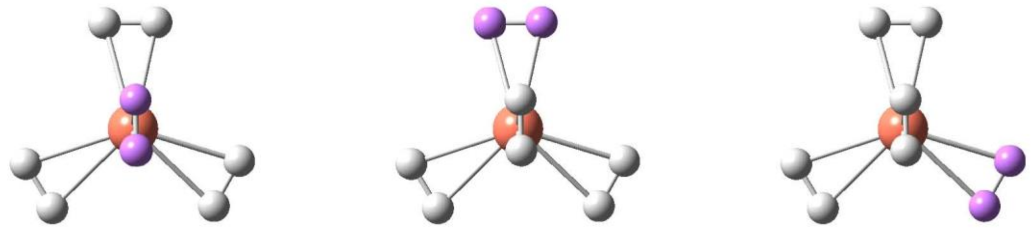


Fig. S5 IRPD spectra of $Cu^+(D_2)_3H_2$. The spectra were measured at both $Cu^+(D_2)_3$ ($Cu^+(D_2)_3H_2$ –> $Cu^+(D_2)_3$ + H_2) and $Cu^+(D_2)_2H_2$ ($Cu^+(D_2)_3H_2$ –> $Cu^+(D_2)_2H_2$ + D_2) fragment channels (black) and only $Cu^+(D_2)_3$ fragment channel (red).



(a) p-a (b) p-b (c) p-c

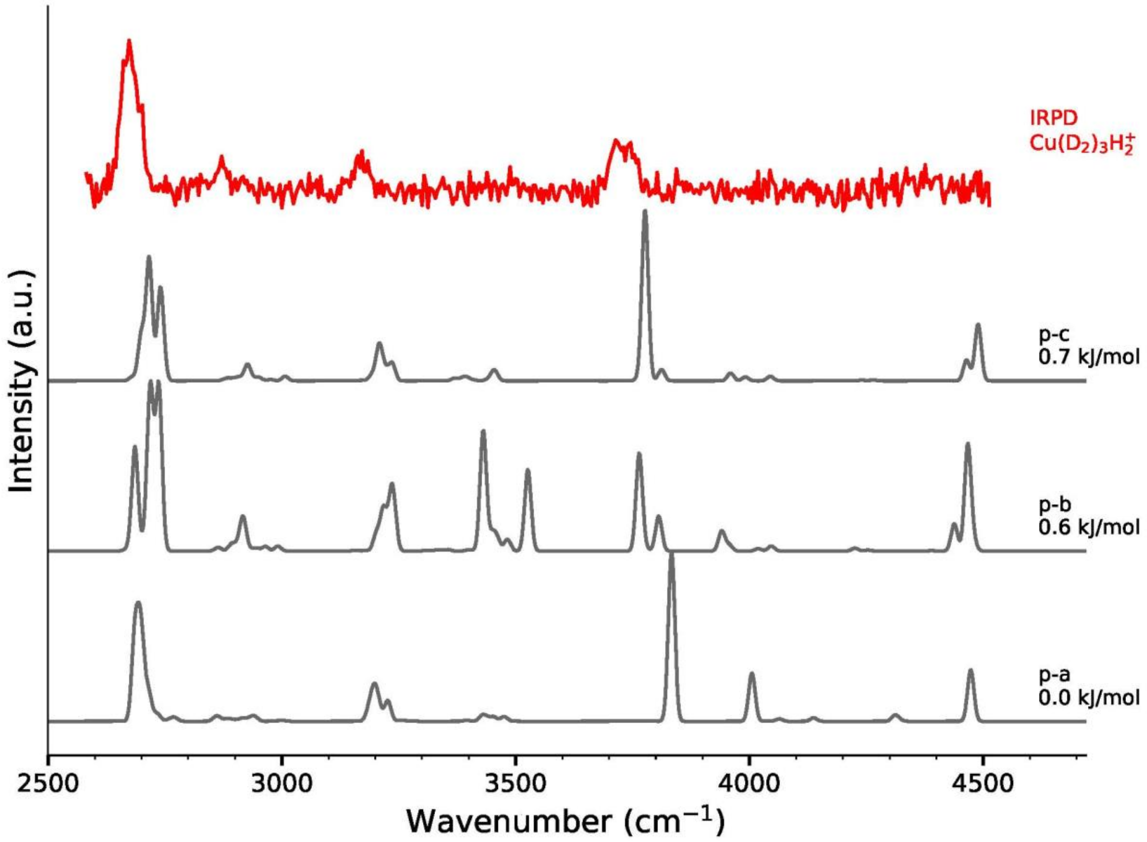


Fig. S6 Experimental and simulated vibrational spectra for the Cu$^+$(D$_2$)$_3$H$_2$. Cu$^+$(H$_2$)$_4$, **C_s-1** has three unique H$_2$ bonding positions. Three simulated spectra and their relative energies (in kJ/mol) are shown in the figure. The isotopomers p-a, p-b and p-c for Cu$^+$(D$_2$)$_3$H$_2$ are also shown in the figure. The position for H$_2$ is labelled in purples. The simulated VPT2 spectra were calculated at MP2/def2-TZVPP level (20 cm^{-1} wide Gaussian lineshape profile).

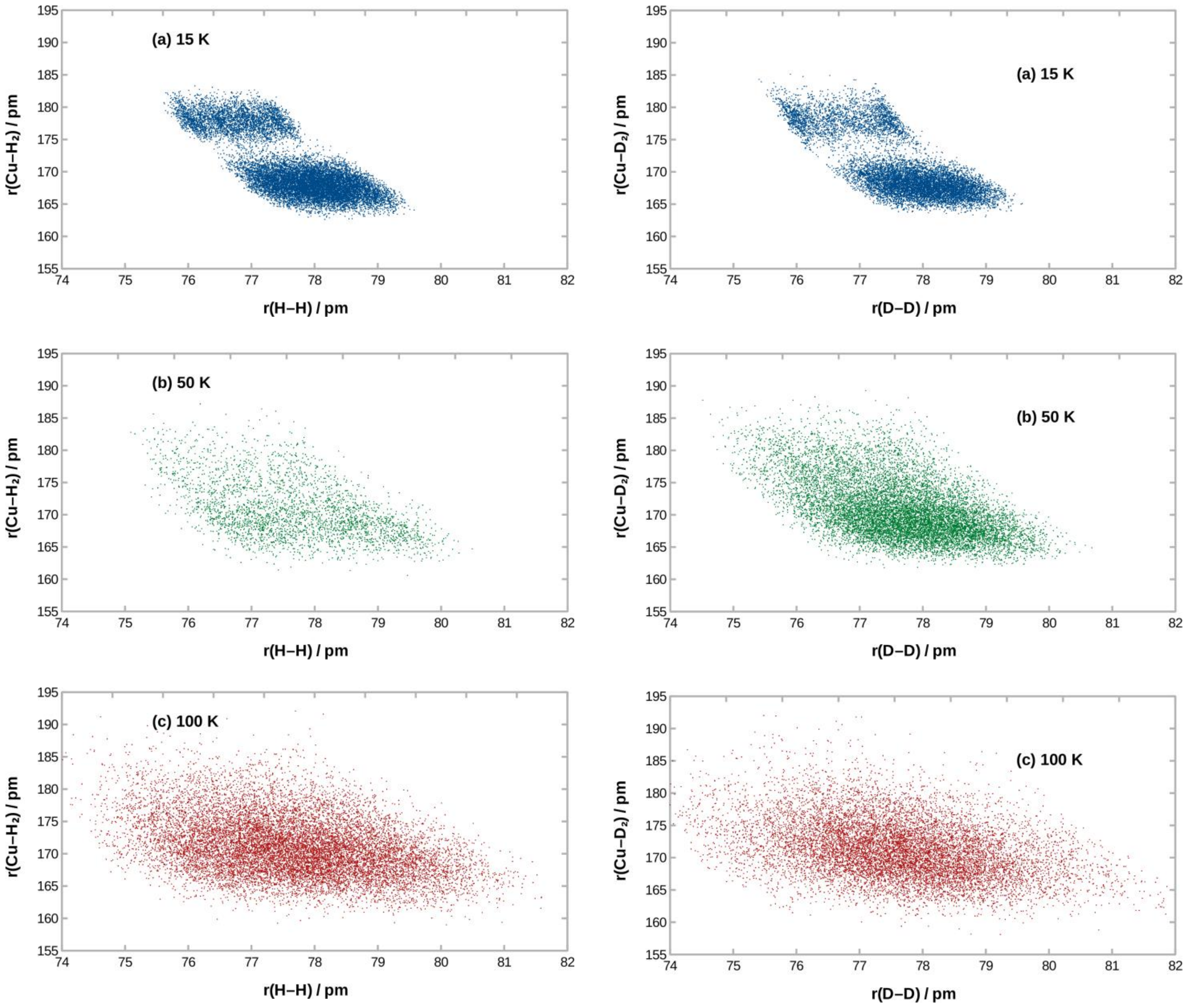


Fig. S7 Correlation between (left:) H–H and Cu–H_2 distance in $Cu^+(H_2)_4$ and (right:) D–D and Cu–D_2 distance in $Cu^+(D_2)_4$ in MD simulations at different temperatures.

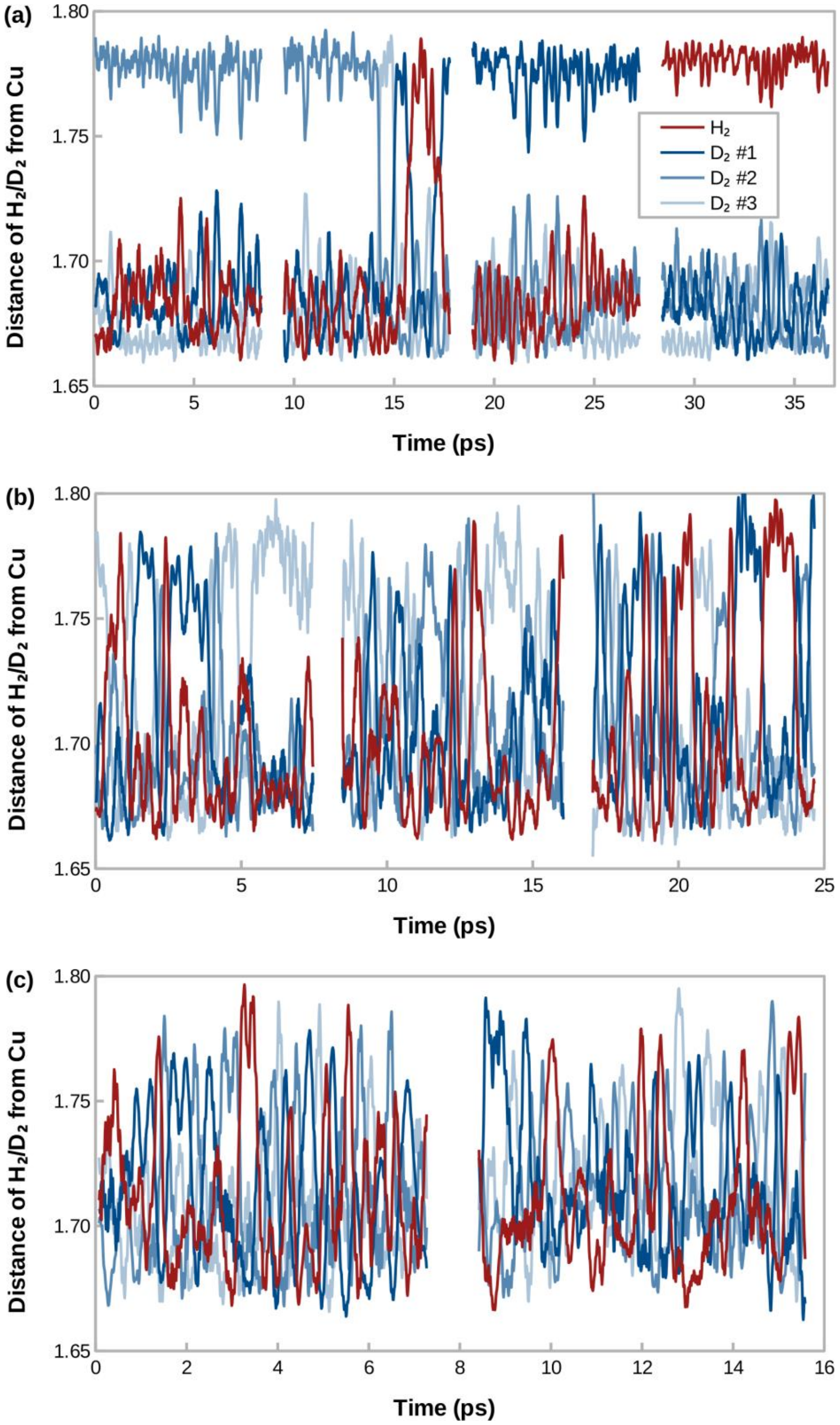


Fig. S8 Distance of centers of the individual H_2 and D_2 molecules to the Cu^+ center along the trajectory of MD simulations for $Cu^+(H_2)(D_2)_3$ at (a) 15 K, (b) 50 K and (c) 100 K. Gaps in the plots indicate independent MD trajectories.

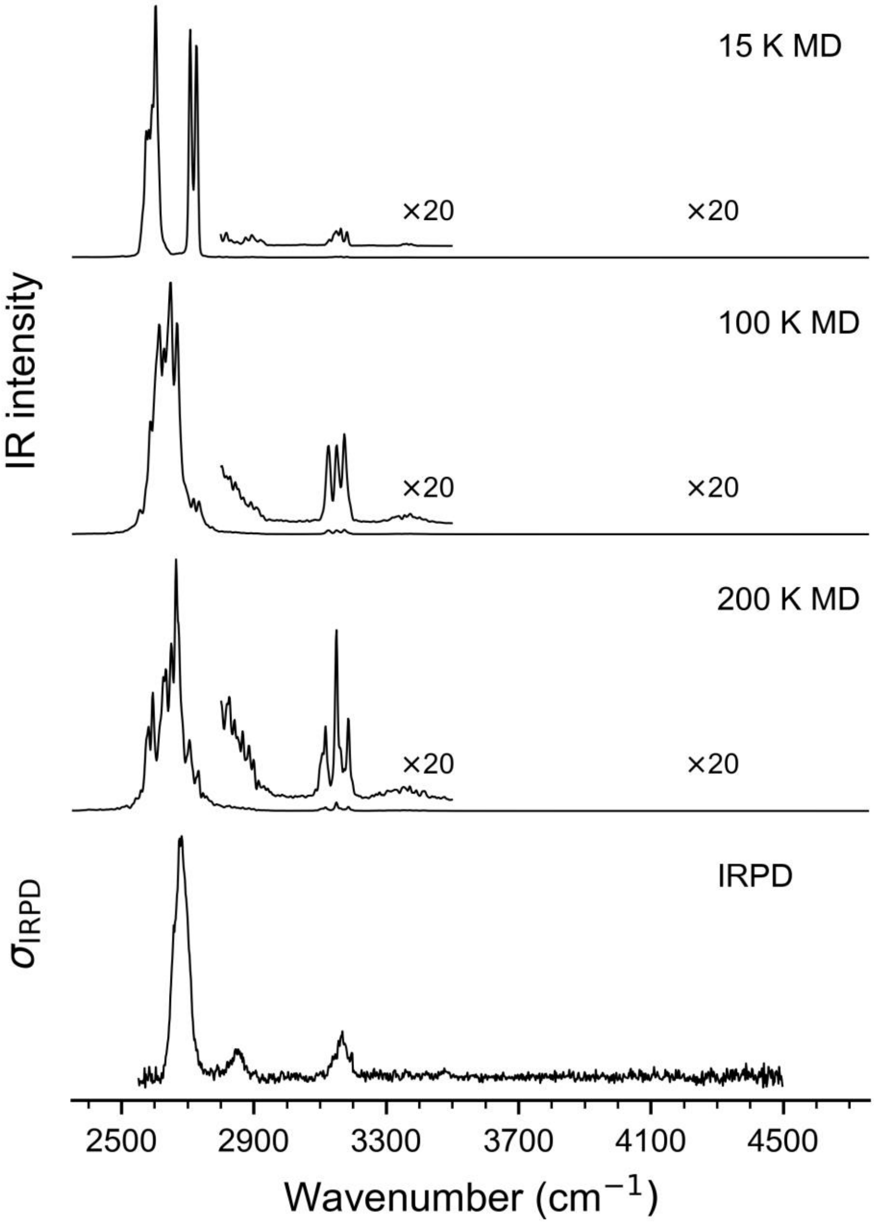


Fig. S9 Comparison of experimental and calculated vibrational spectra of $Cu^+(D_2)_4$: BOMD IR spectra at 15 K, 100 K and 200 K (all scaled by 0.932), and experimental IRPD spectrum.