Rotational spectrum and non-covalent interaction of isopropylamine-water, an adduct of a potential interstellar molecule

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INTRODUCTION

Organoamines have been drawn considerable attention in material sciences and nano-technology areas, and many organoamines are also detected in interstellar space. Isopropylamine ($CH_3CH(NH_2)CH_3$) is a potential interstellar molecule in space. Here, the water adduct of isopropylamine was investigated by supersonic jet Fourier transform microwave spectroscopy, which is a powerful tool for the most detailed structural picture of the molecules or clusters. Two isomers stabilized by classic hydrogen bond (O-H⋯N) and weak hydrogen bond (C-H⋯O) were observed in supersonic expansion. Transition frequencies, conformational composition, rotational constants and ^{14}N nuclear quadrupole coupling constants of the adduct have been provided.

Theoretical calculations

Tab. 1 Theoretical shapes and spectroscopic parameters (relative zero-point energy ΔE_0, rotational constants A/B/C, dipole moment $\mu_a/\mu_b/\mu_c$ and nuclear quarudpole coupling constants χ_{aa}, χ_{bb}-χ_{cc}) of the isopropylamine-water adduct at B2PLYP-D3BJ/aug-cc-pVTZ-dH level of theory.

	trans	gauche
Isomer		
	trans	*gauche*
ΔE_0 [cm^{-1}]	0	131
A,B,C [MHz]	4873, 2569, 2477	7329, 2146, 1836
μ_a, μ_b, μ_c [D]	1.7, 0.0, -2.6	2.2, -1.9, -1.1
χ_{aa}, χ_{bb}-χ_{cc} [MHz]	-3.0, 0.88	-4.1, -0.16

Rotational spectrum

Fig. 1 Supersonic-jet Fourier transform microwave spectrometer, covering **2.0-20.0 GHz**, and its work principle.
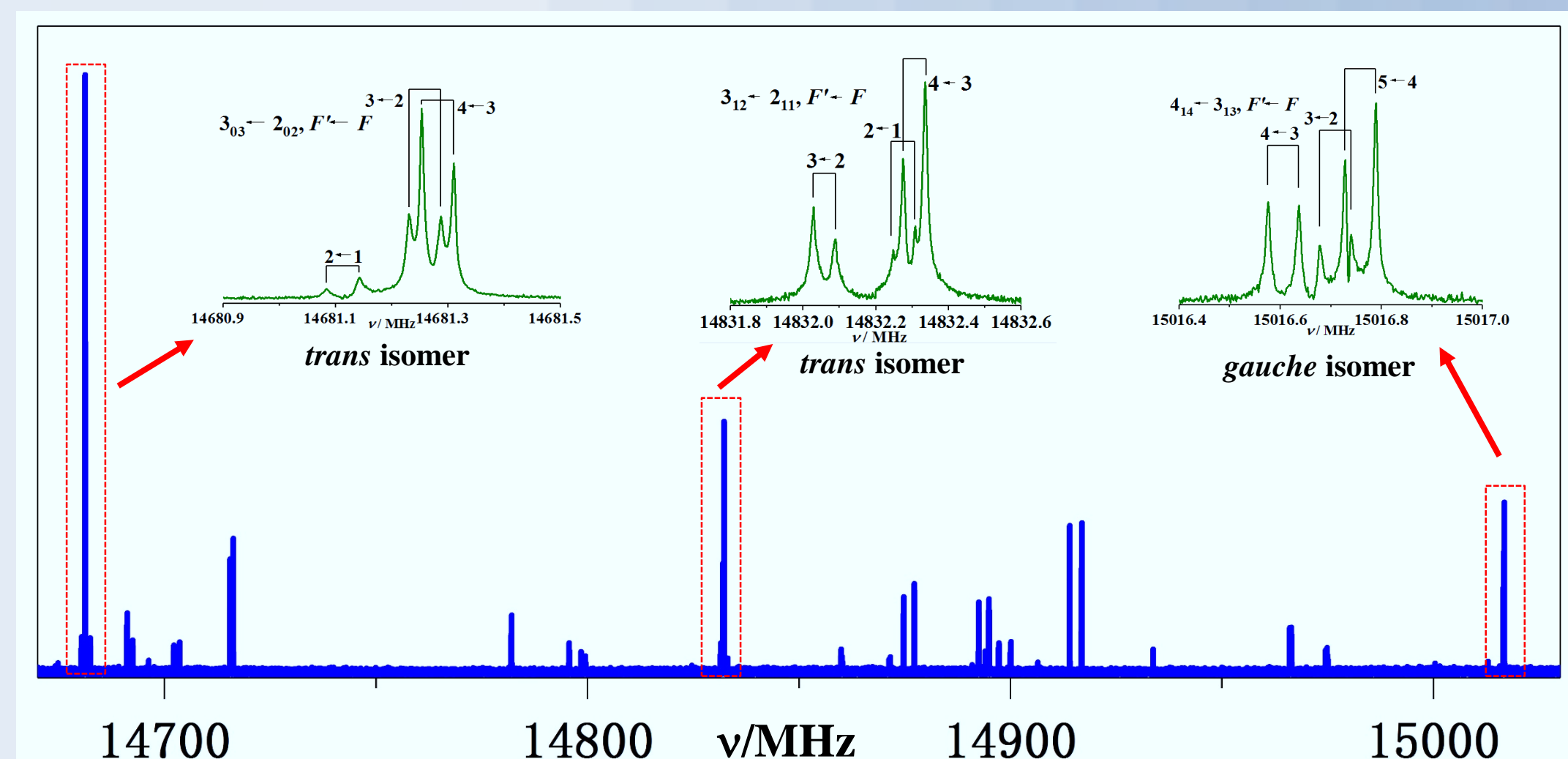
Fig. 2 The recorded partial transitions of the both isomers. The transitions display the ^{14}N nuclear hyperfine structure. Each line exhibits the Doppler doubling. Experiment condition: sample concentration: ~ **1%** in He (or Ar); stagnation pressure: **~0.1 MHz**.

Results and discussion

Tab. 2 Experimental spectroscopic parameters of the observed two isomers of the normal species and water isotopologues. (* All centrifugal distortion parameters are not listed in the following tables.)

	trans	gauche
A [MHz]	4880.478(2)	7271.1051(8)
B [MHz]	2496.0733(7)	2102.8264(2)
C [MHz]	2401.5471(6)	1805.9595(2)
χ_{aa} [MHz]	-2.730(3)	-3.82(1)
(χ_{bb}-χ_{cc})[MHz]	0.732(4)	-0.128(4)
N	52	54
σ [kHz]	3.1	2.4

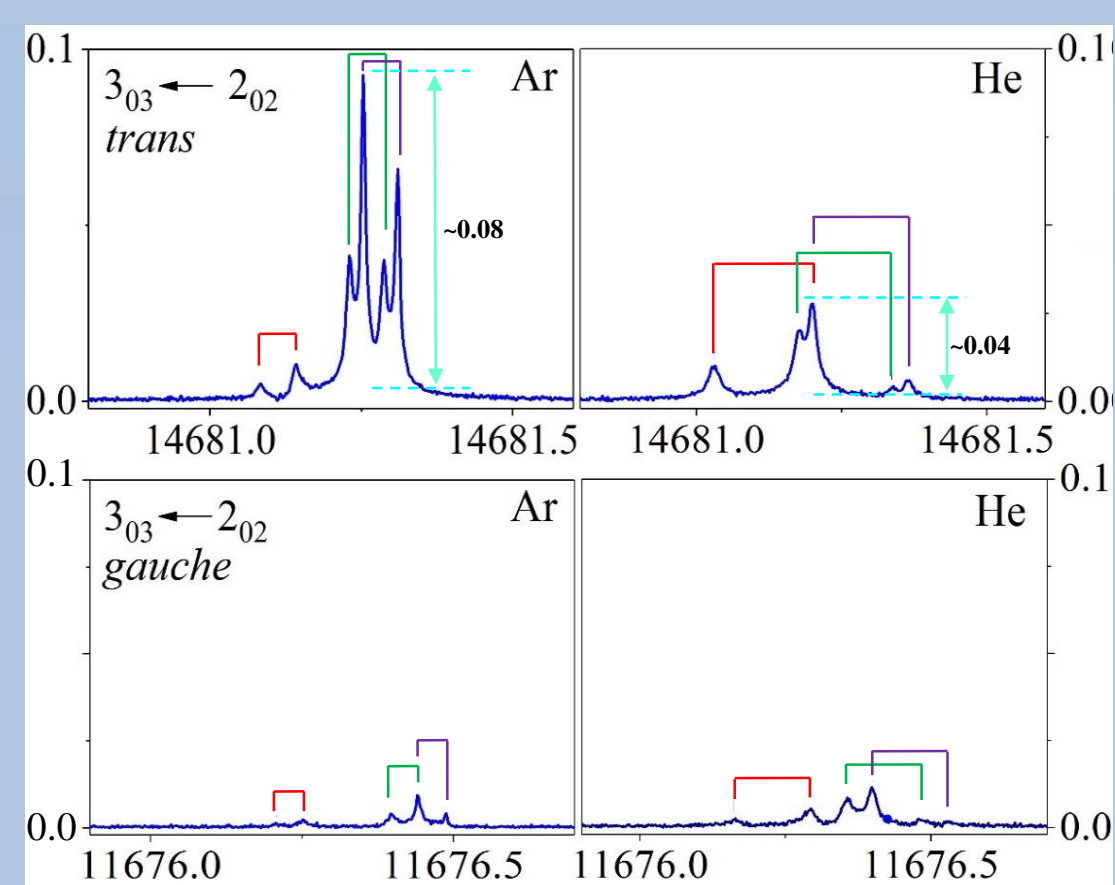| trans	t-H$_2^{18}$O	t-DOH	t-HOD
A [MHz]	4869.612(1)	4876.914(2)	4870.200(4)
B [MHz]	2360.8805(6)	2463.525(1)	2384.165(1)
C [MHz]	2278.5259(5)	2372.066(1)	2298.261(1)
χ_{aa} [MHz]	-2.799(5)	-2.71(1)	-2.74(1)
(χ_{bb}-χ_{cc})[MHz]	0.636(4)	0.67(1)	0.57(1)
N	45	37	31
σ [kHz]	2.6	3.5	2.9
gauche	g-H$_2^{18}$O	g-DOH	g-HOD
A [MHz]	7258.808(1)	7257.832(1)	7229.068(1)
B [MHz]	1982.1054(3)	2072.5464(3)	2010.6607(2)
C [MHz]	1716.8403(3)	1782.3212(3)	1737.4055(2)
χ_{aa} [MHz]	-3.85(2)	-3.81(2)	-3.79(1)
(χ_{bb}-χ_{cc})[MHz]	-0.136(8)	-0.14(1)	-0.372(8)
N	44	44	35
σ [kHz]	2.4	2.7	1.9

Fig. 3 The relative intensity for transition of *trans* isomer in Ar is **about twice** as strong as that in He, while the intensity of *gauche* isomer in Ar is **less than** that in He, which allowed estimating the relative population ratio as N_t:N_g ≈ 3:1.
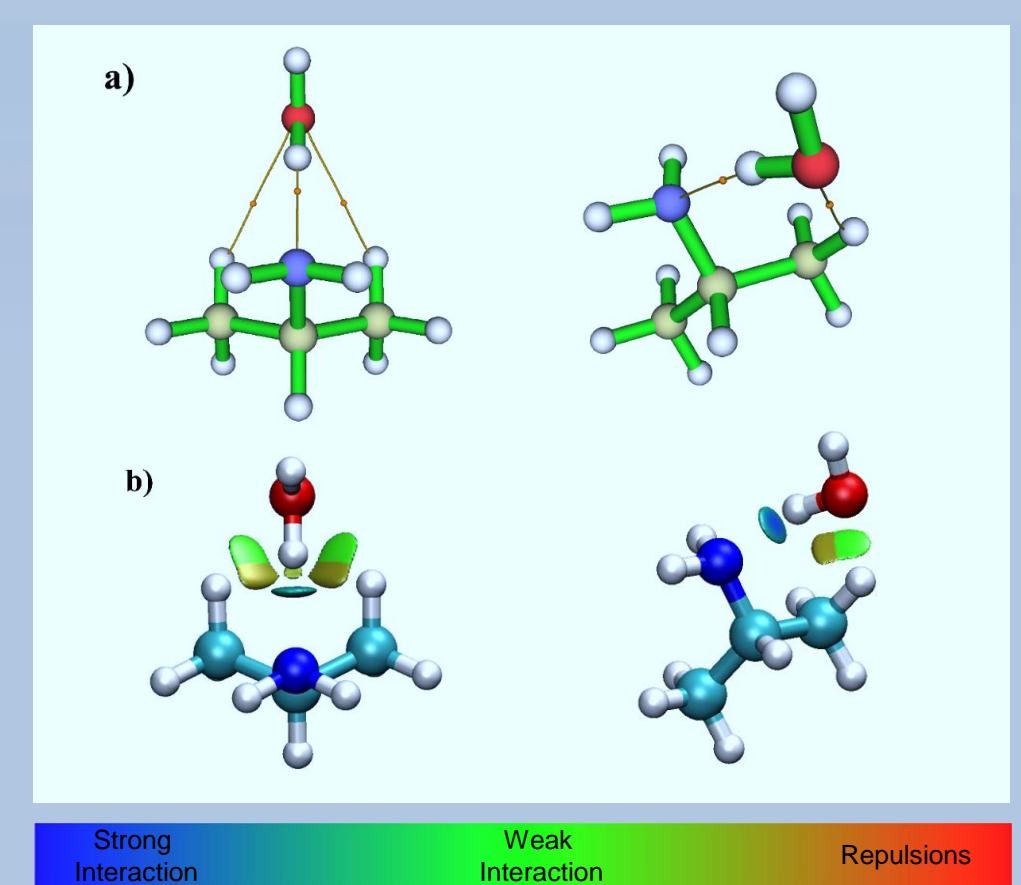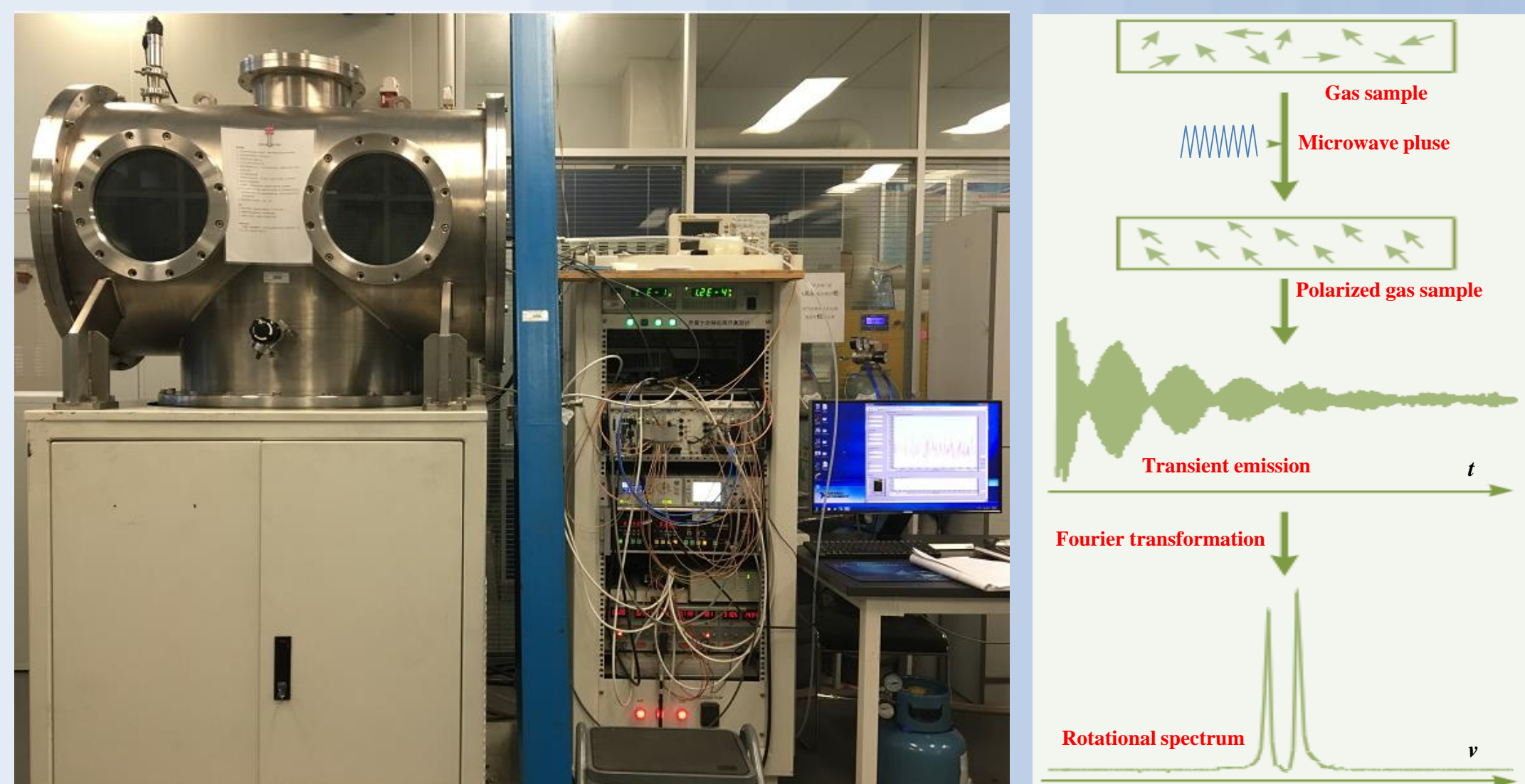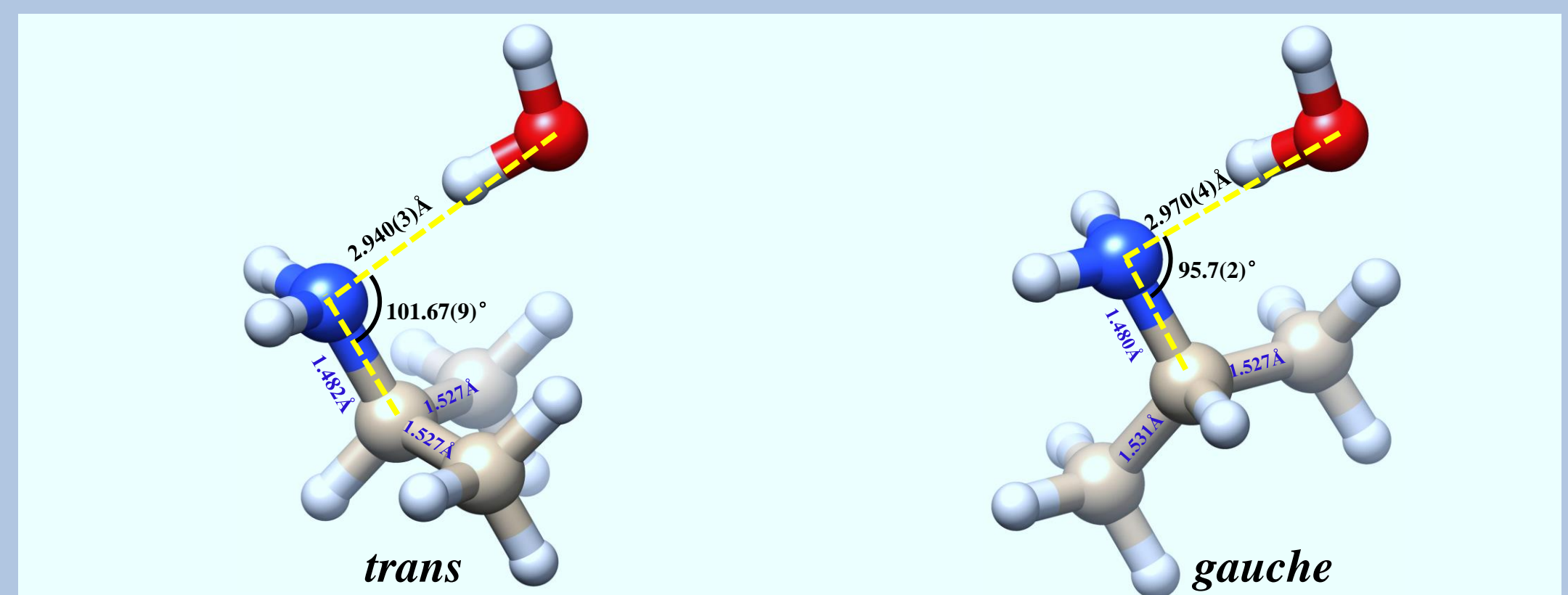

Fig. 4 Results of QTAIM and NCI analyses. a) three and two bond critical points (red dolts) are indentified in *trans* and *gauche* isomers, respectively; b) the NCI isosurfaces calculated at the B2PLYP-D3BJ/aug-cc-pVTZ-dH level of theory

Fig. 5 Experimental (r_0) structures of the observed isomers. The distances R_{ON} and angles $\angle$ONC in both isomers were adjusted while keeping the remaining parameters fixed to their theoretical values (r_e) to reproduce all experimental rotational constants.

Tab. 3 SAPT analysis for the isopropylamine-water adduct in comparison with $(H_2O)_2$ (All values in kJ mol^{-1})

Adduct	Electrostatics	Induction	Dispersion	Exchange	Total
$(H_2O)_2$	-34.3	-10.2	-9.4	35.2	-18.7
trans	-60.4	-20.0	-18.2	62.6	-36.1
gauche	-59.7	-19.9	-16.6	60.6	-35.6

CONCLUSIONS

- Two isomers of the isopropylamine-water adduct held together by classic hydrogen bond (O-H⋯N) and weak hydrogen bond (C-H⋯O) were observed.
- The rotational constants, transition frequencies and ^{14}N nuclear quadrupole coupling constants for two isomers were accurately measured.
- The intensity measurements in He or Ar reveal the *trans* isomer is more stable than *gauche* one (relative population ratio: N_t:N_g ≈ 3:1).