

Characteristics of Hydrogen Bonding between Chalcogen and Pnictogen Species

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Hydrogen bonding is one of the most prevalent types of intermolecular interactions in nature. While many O–H...B and O...H–A systems have been investigated, complexes involving non-oxygenated N–R₃ and sulfur-based molecules *exclusively* have been received less attention... We conducted matrix isolation Fourier transform infrared (MI-FTIR) spectroscopy studies using gas mixtures of argon, H₂S and several nitrogen species in order to investigate these interactions.

H₂S • NH₃

Hydrogen sulfide (H₂S) and ammonia (NH₃) are emitted into the atmosphere through both natural and anthropogenic processes, yet their interaction is largely unexplored. This is particularly surprising, as NH₄SH ice clouds are believed to be responsible for the colour of Jupiter's Great Red Spot,¹ which has not yet been fully explained.

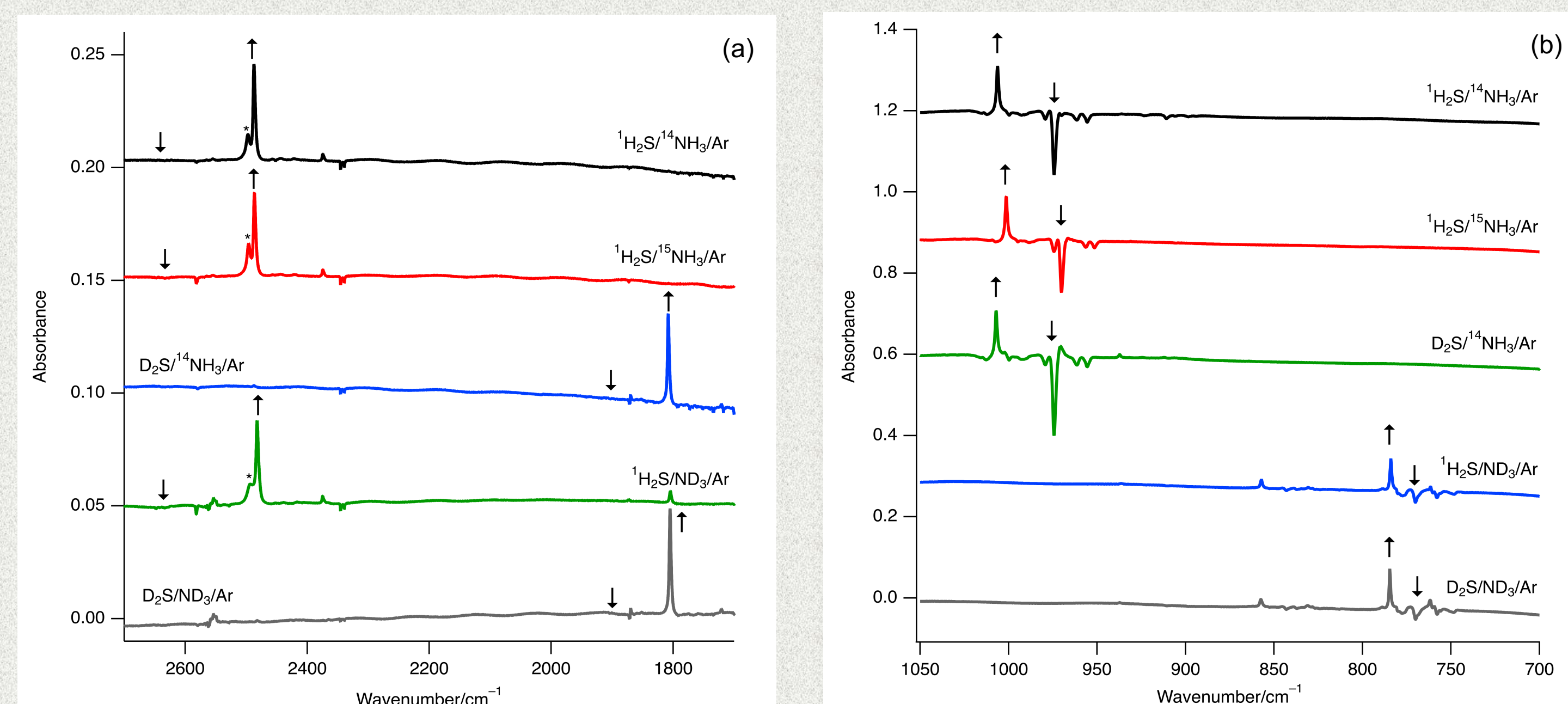


Figure 1: MI-FTIR difference spectra of mixtures containing various isotopologues of H₂S and NH₃ in solid argon. Spectra were recorded following deposition at 10 K. The spectra in (a) show the ν_1 and ν_3 stretching regions of H₂S, while the spectra in (b) show the ν_2 'umbrella' vibration region of NH₃.²

Table 1: Frequency shifts (in cm⁻¹) as a result of complexation between H₂S and NH₃ with respect to monomer vibrational frequencies.²

Vibration	¹ H ₂ S• ¹⁴ NH ₃	¹ H ₂ S• ¹⁵ NH ₃	D ₂ S• ¹⁴ NH ₃	¹ H ₂ S•ND ₃	D ₂ S•ND ₃
NH ₃ , ν_2	+ 31.8	+ 31.3	+ 32.7	+ 23.9	+ 24.5
H ₂ S, ν_2	+ 15.1	+ 15.0	+ 11.1		
NH ₃ , ν_4 (sym)	– 21.1	– 21.0		– 8.1	– 7.7
NH ₃ , ν_4 (asym)	– 6.8	– 6.8			
H ₂ S, ν_1	– 155.3	– 156.0	– 105.8	– 160.3	– 108.9
H ₂ S, ν_1^*	– 145.4	– 146.4		– 148.9	
NH ₃ , ν_1	– 21.5	– 22.1	– 22.3		
NH ₃ , ν_3 (sym)	– 24.1	– 24.3	– 24.2		
NH ₃ , ν_3 (asym)	– 13.4	– 13.5	– 13.9		

Splitting of the ν_1 vibration of ¹H₂S upon complexation indicates the presence of two different trapping sites; the absence of the splitting in the D₂S/NH₃ spectra suggests that in one site (marked *), the ¹H₂S subunit undergoes hindered rotation, **tunnelling through the Ar matrix**, while, in the other site, the rotation is completely suppressed.²

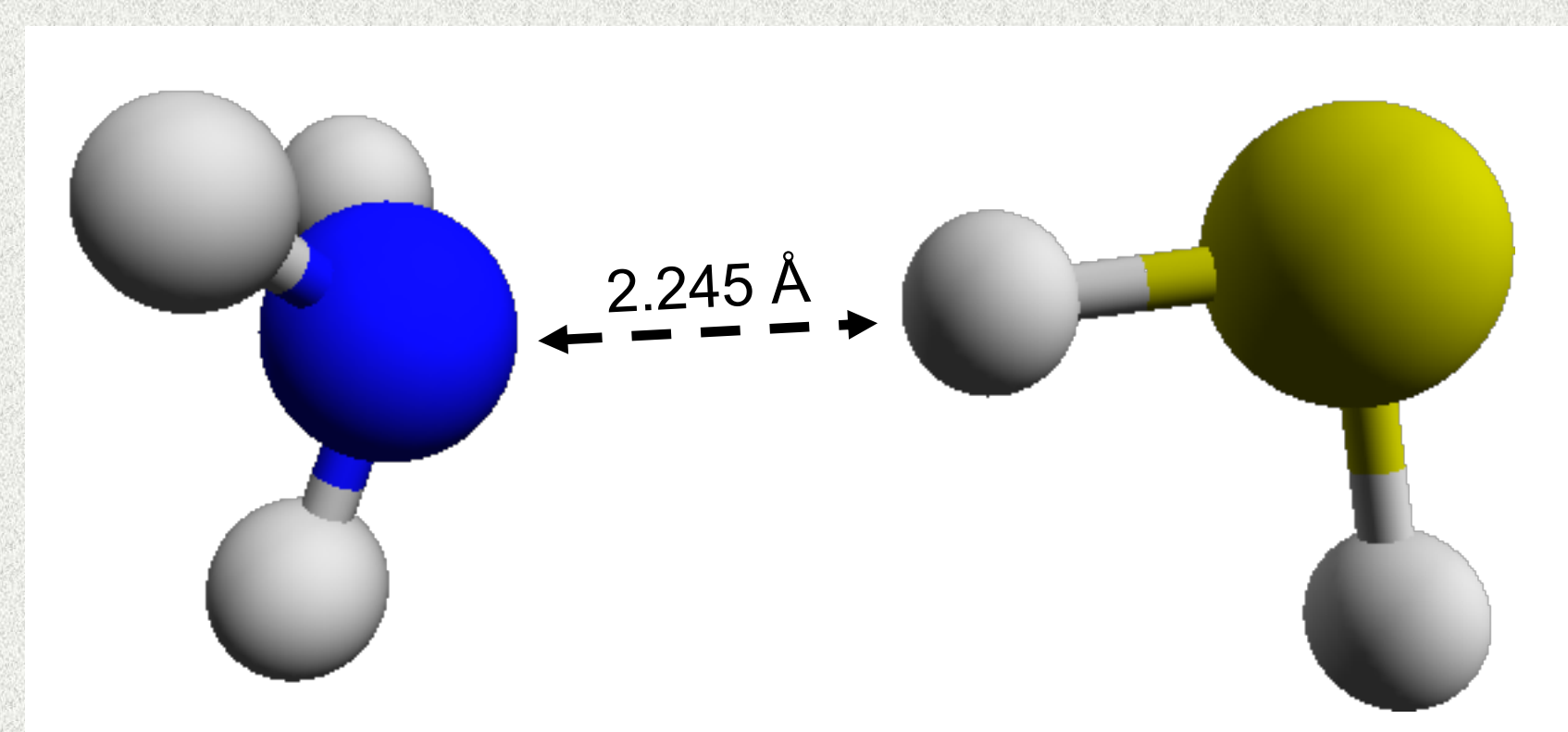


Figure 2: The H₂S•NH₃ complex, optimised at CCSD(T)/aug-cc-pV(T+d)Z level of theory.

H₂O • PH₃

PH₃ is considered a biosignature gas in the search for extra-terrestrial life in anoxic environments.⁸ Surprisingly, the 1:1 H₂O•PH₃ complex had not been investigated, despite the importance of H₂O for the propagation of life. We sought to rectify this using MI-FTIR to identify the complex.

A binding energy of 5.1 kJ mol⁻¹ was calculated at CCSD(T)/CBS_{T,Q,5} level of theory; much weaker than its S/N analogue, H₂S•NH₃, with 8.6 kJ mol⁻¹ at the same level of theory.²

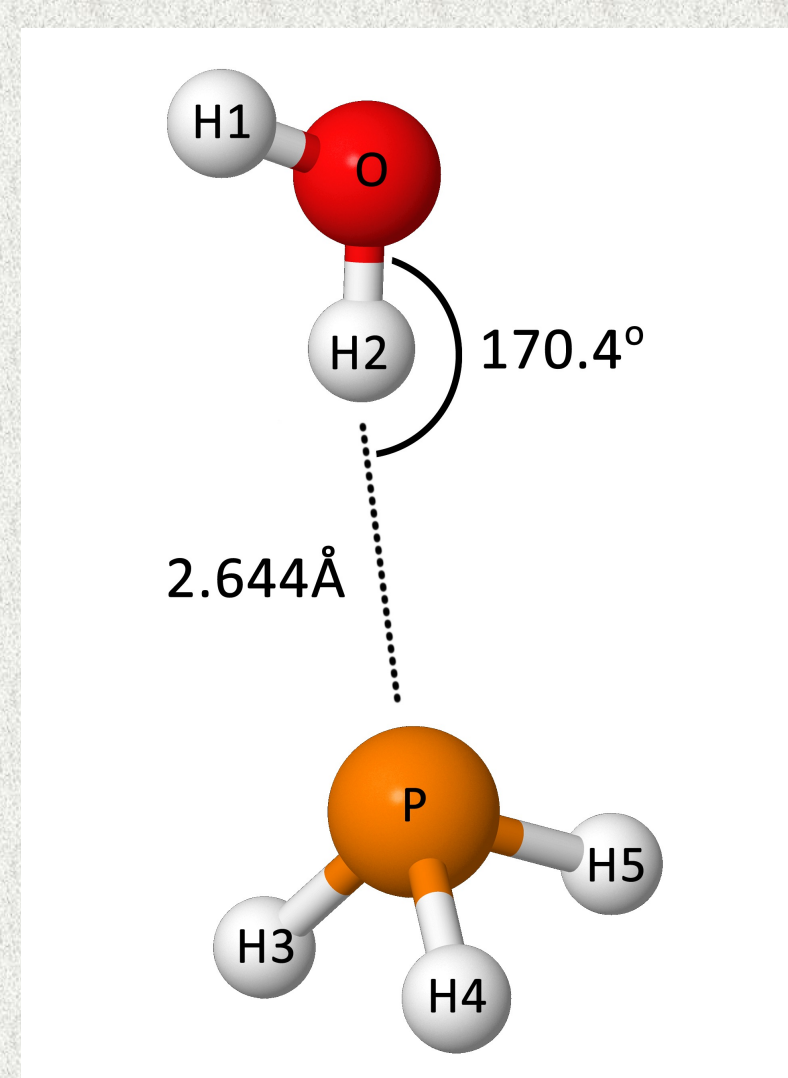


Figure 5: The H₂O•PH₃ complex, optimised at CCSD(T)/aug-cc-pV(T+D)Z level of theory.

H₂S • Amines

Clouds have a significant effect on global energy uptake in the atmosphere. The presence and behaviour of clouds is largely dependent on cloud condensation nuclei (CCN)³ – hydrophilic aggregates of atmospheric particles upon which water vapour can condense. CCN generally include sulfur-containing molecules, such as H₂SO₄.⁴ It has recently been found that nitrogen-containing molecules, including NH₃, methyl-, dimethyl-, and trimethylamine (MA, DMA, TMA, respectively) significantly enhance the ability of H₂SO₄ to attract water molecules.⁵ We looked at the interactions between these amines and H₂S, the sulfur analogue of H₂O, in order to explore the interactions between sulfur and nitrogen-containing species and create a 'series' of data which could be used to predict the binding of other such molecules.

The binding energy of the complex can be qualitatively estimated by the shift in the ν_1 vibration of H₂S. **The trend determined from our spectra (DMA > TMA > MA) does not match that of the gas phase (GP) basicity data, nor does it match our calculated values** (see Figure 3, Table 2). This *may* be due to interference from the Ar matrix. We are in the process of investigating this possibility.

New peaks appear at higher energy wavelengths to each H₂S•amine peak (see Figure 3). They are present in every H₂S•amine spectrum. Their origins are currently unknown.

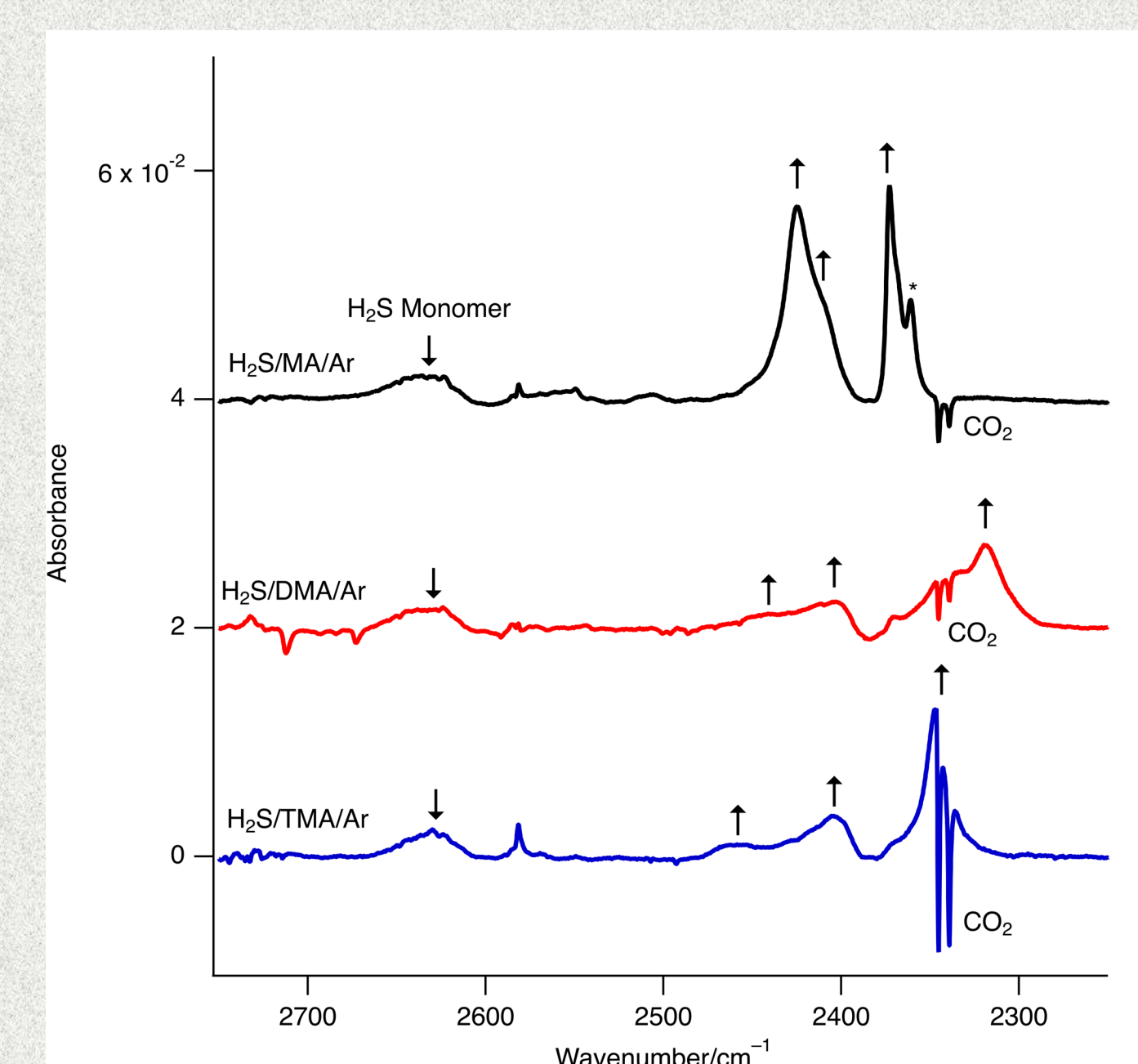


Figure 3: MI-FTIR difference spectra of mixtures containing H₂S and MA, DMA or TMA in solid argon. Spectra were recorded following deposition at 10 K.

Table 2: Comparison of data related to MA, DMA and TMA or their complexes with H₂S.

Complex	$\Delta\nu_1$ (H ₂ S)	Amine Basicity, kJ mol ⁻¹ (GP) ⁶	Amine Basicity (Aq., pK _{aH}) ⁷	Binding Energy (kJ mol ⁻¹)*
¹ H ₂ S•NH ₃	–155.3	819.0		7.3
¹ H ₂ S•MA	–263.8	864.5	10.62	12.4
¹ H ₂ S•DMA	–305.8	896.5	10.64	14.6
¹ H ₂ S•TMA	–277.8	918.1	9.76	15.4

*CCSD(T)-RI/F12/AVQZ-F12//B97M-D4/AVQZ

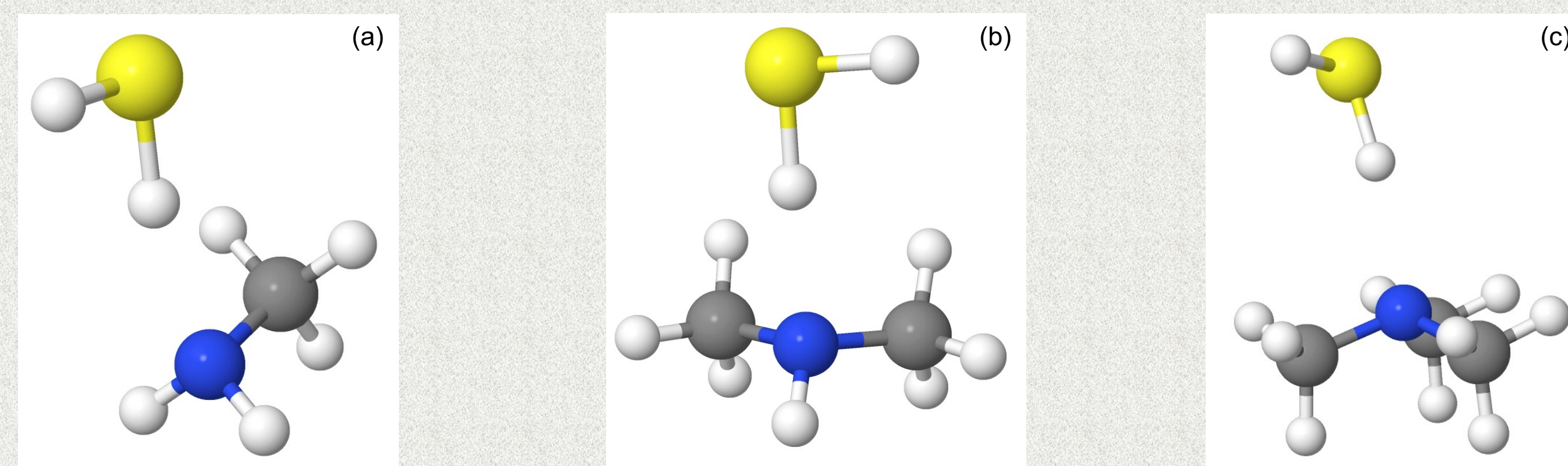


Figure 4: Most tightly bound conformers calculated for the H₂S•amine complexes. The structure in (a) is of the H₂S•MA complex, calculated at CCSD(T)/aug-cc-pV(T+d)Z level of theory. The structures in (b) and (c) are of the H₂S•DMA and H₂S•TMA complexes, respectively, calculated at B97M-D4/aug-cc-pV(Q+d)Z level of theory.

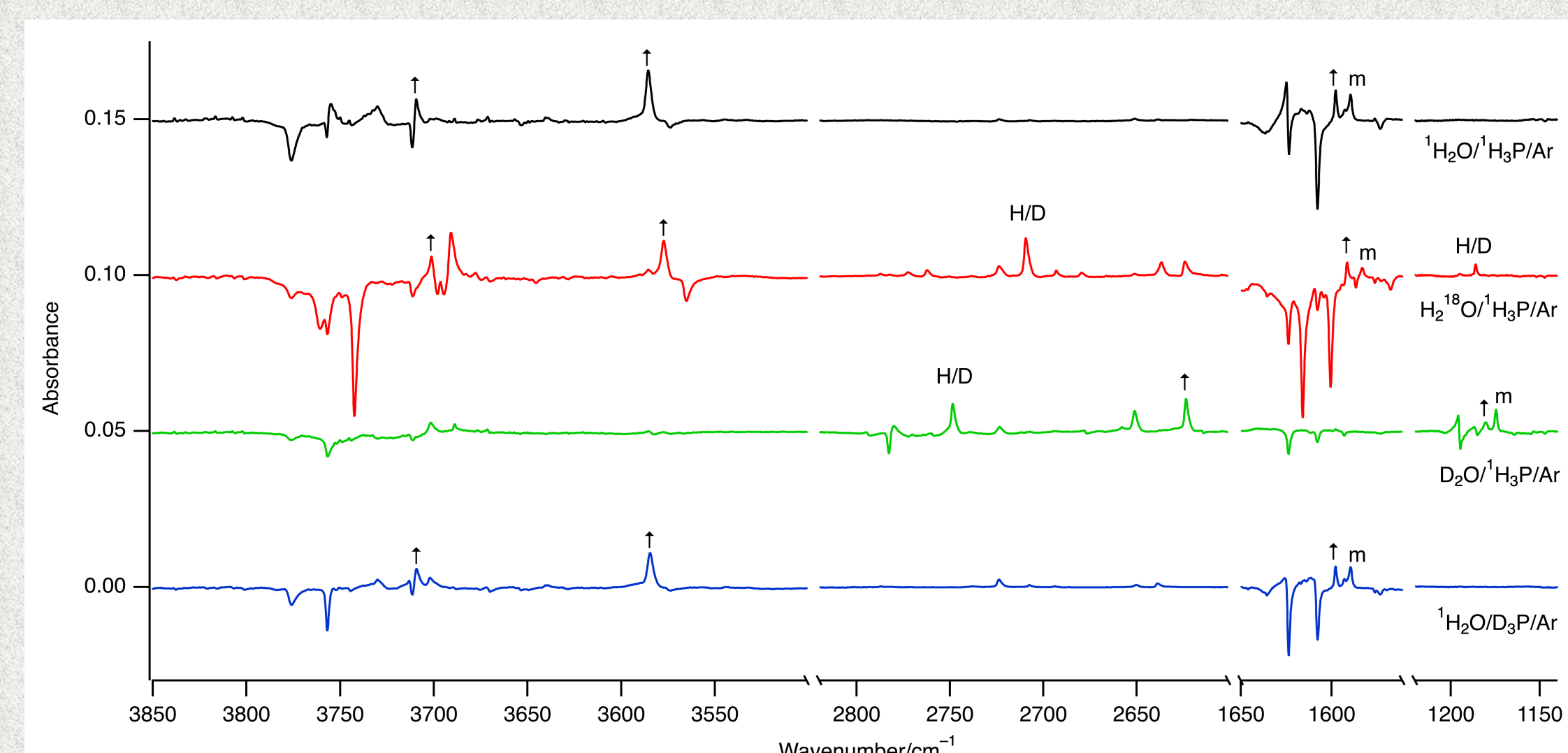


Figure 6: MI-FTIR difference spectra of mixtures containing different isotopologues of H₂O and PH₃ in Ar matrices.

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