

Infrared and Raman spectra of the MoS₂-adenine and MoS₂-guanine complexes: a DFT/M06-2X study

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The main aim of this work is to determine the effect of interaction with molybdenum disulfide on the vibrational spectra of purine nucleobases: adenine and guanine (Fig. 1), and to identify spectral markers of this interaction for each base. We employed the quantum-mechanical DFT/M06-2X method to calculate the structure, infrared and Raman spectra of the nucleobases with the MoS₂ monolayer. The calculations were performed for the complexes with the pristine MoS₂ fragment as well as with the MoS₂ fragment having point surface defects.

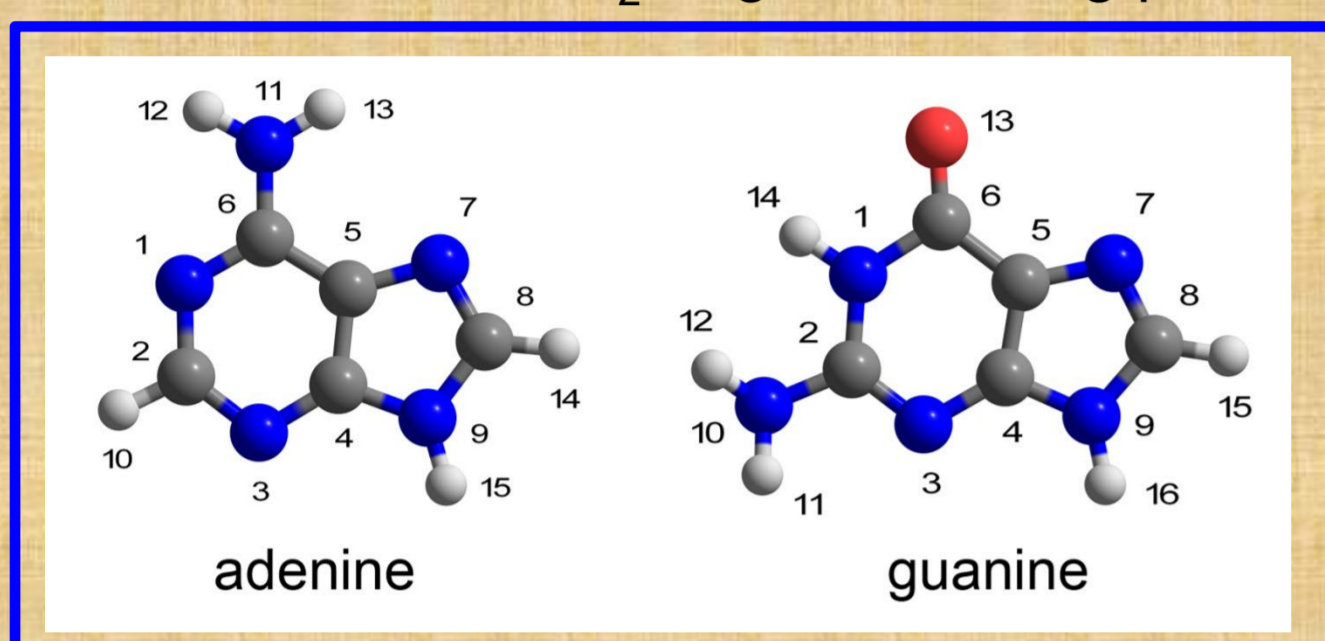


Fig. 1. Structure of adenine and guanine molecules (dark grey - carbon, blue - nitrogen, red - oxygen, grey - hydrogen).

Complexes of adenine and guanine with MoS₂ having point surface defects. Structure and interaction energies

Calculations were performed for adenine and guanine complexes with a MoS₂ fragment containing two types of the surface point defects. The first type is the substitution of a surface sulfur atom by a molybdenum atom (denoted as Mo_S). The second defect involves removing two adjacent surface sulfur atoms (denoted as V_{2S}). Both defects provide an opportunity to form additional covalent bonds with the guest molecules. Structure and interaction energies of all calculated complexes are shown in Fig. 2.

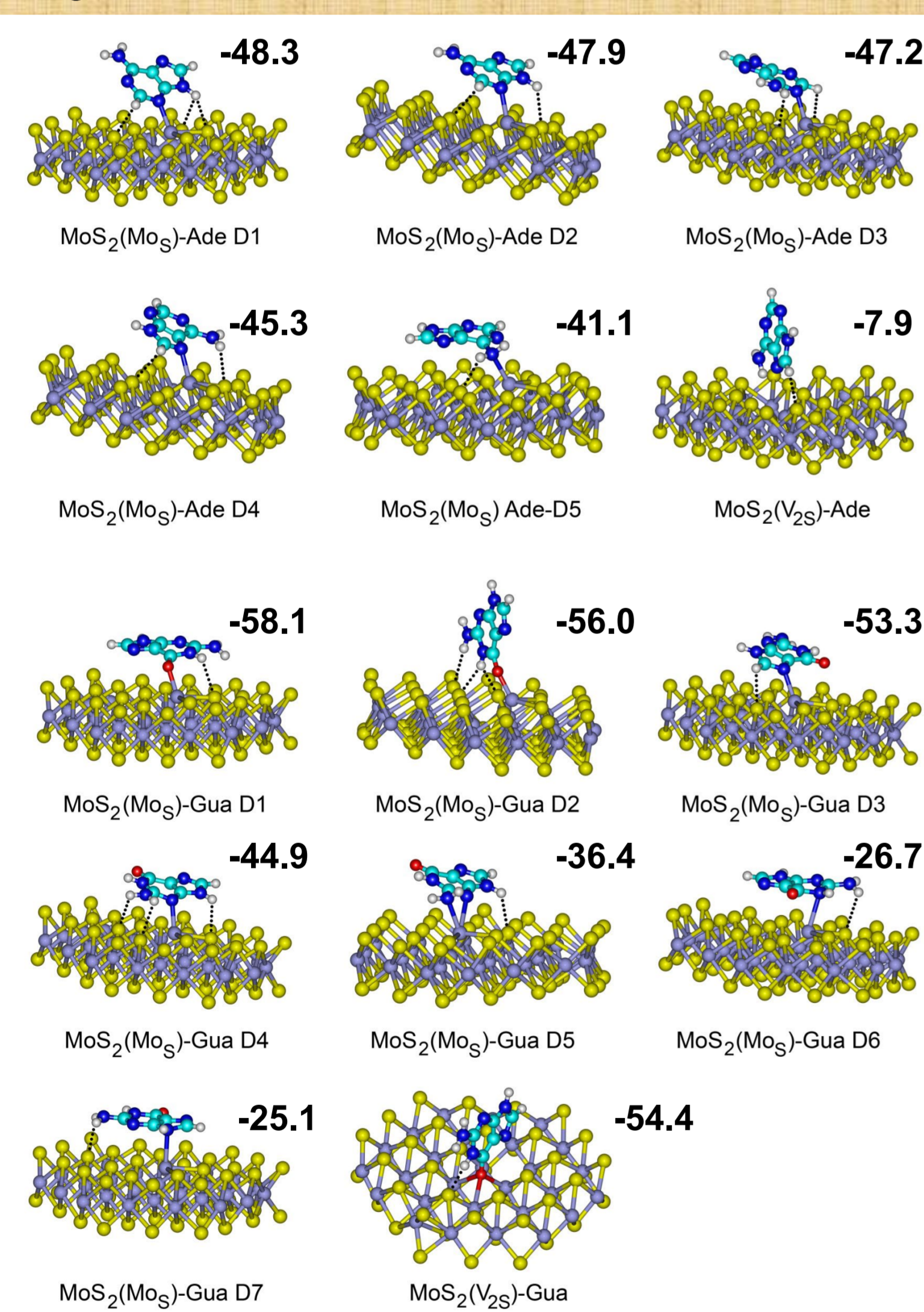


Fig. 2. Complexes of adenine and guanine with MoS₂ having point defects. Interaction energies in kcal/mol.

Calculations revealed the existence of six adenine and seven guanine complexes with MoS₂ containing the Mo_S defect. In these complexes, a coordination bond is formed between the surface Mo atom and the nitrogen or oxygen atoms of the bases. The interaction energies depend significantly on the type of base atom that forms the bond with MoS₂. The strongest interaction is observed for two guanine complexes in which the bond is formed by the oxygen atom. The total interaction energy in the calculated complexes is determined by the energy of the coordination bonds,

as well as by the presence of stacking interactions and NH...S hydrogen bonds.

Calculations of complexes with the V_{2S} defect revealed significant differences in the interaction energies for adenine and guanine. This is explained by the fact that the adenine molecule lacks atoms capable of forming strong coordination bonds with the internal molybdenum atoms. At the same time, the oxygen atom of guanine forms coordination bonds with three internal molybdenum atoms. To quantitatively describe the coordination bonds, we calculated the Wiberg bond indices (WBI) for all the complexes calculated (Table 1). The obtained results demonstrate a relationship between interaction energies and the WBI. Values of WBI are approximately 0.4–0.5 for the most stable complexes. This confirms the formation of covalent coordination bonds in the complexes.

Table 1. Wiberg bond indexes (WBI) of the MoS₂-Ade and MoS₂-Gua complexes

Complex	Bond	WBI	Complex	Bond	WBI
MoS ₂ (Mo _S)-Ade D1	N3-Mo	0.497	MoS ₂ (Mo _S)-Gua D1	O-Mo	0.564
MoS ₂ (Mo _S)-Ade D2	N3-Mo	0.489	MoS ₂ (Mo _S)-Gua D2	O-Mo	0.557
MoS ₂ (Mo _S)-Ade D3	N1-Mo	0.488	MoS ₂ (Mo _S)-Gua D3	N7-Mo	0.449
MoS ₂ (Mo _S)-Ade D4	N7-Mo	0.468	MoS ₂ (Mo _S)-Gua D4	N3-Mo	0.487
MoS ₂ (Mo _S)-Ade D5	N6'-Mo	0.360	MoS ₂ (Mo _S)-Gua D5	N3-Mo	0.281
MoS ₂ (V _{2S})-Ade	N7-Mo*	0.018	MoS ₂ (Mo _S)-Gua D6	N1-Mo	0.185
		0.010	MoS ₂ (Mo _S)-Gua D7	N9-Mo	0.168
		0.009	MoS ₂ (V _{2S})-Gua	O-Mo*	0.286
					0.283
					0.214

IR and Raman spectra

Next, we studied the influence of intermolecular interactions (stacking and coordination bonds) on the vibrational spectra of adenine and guanine. Figs. 3 and 4 present graphical representations of the calculated IR and Raman spectra. The spectra are shown for pristine MoS₂ (Fig. 3) and for MoS₂ with Mo_S defect (Fig. 4).

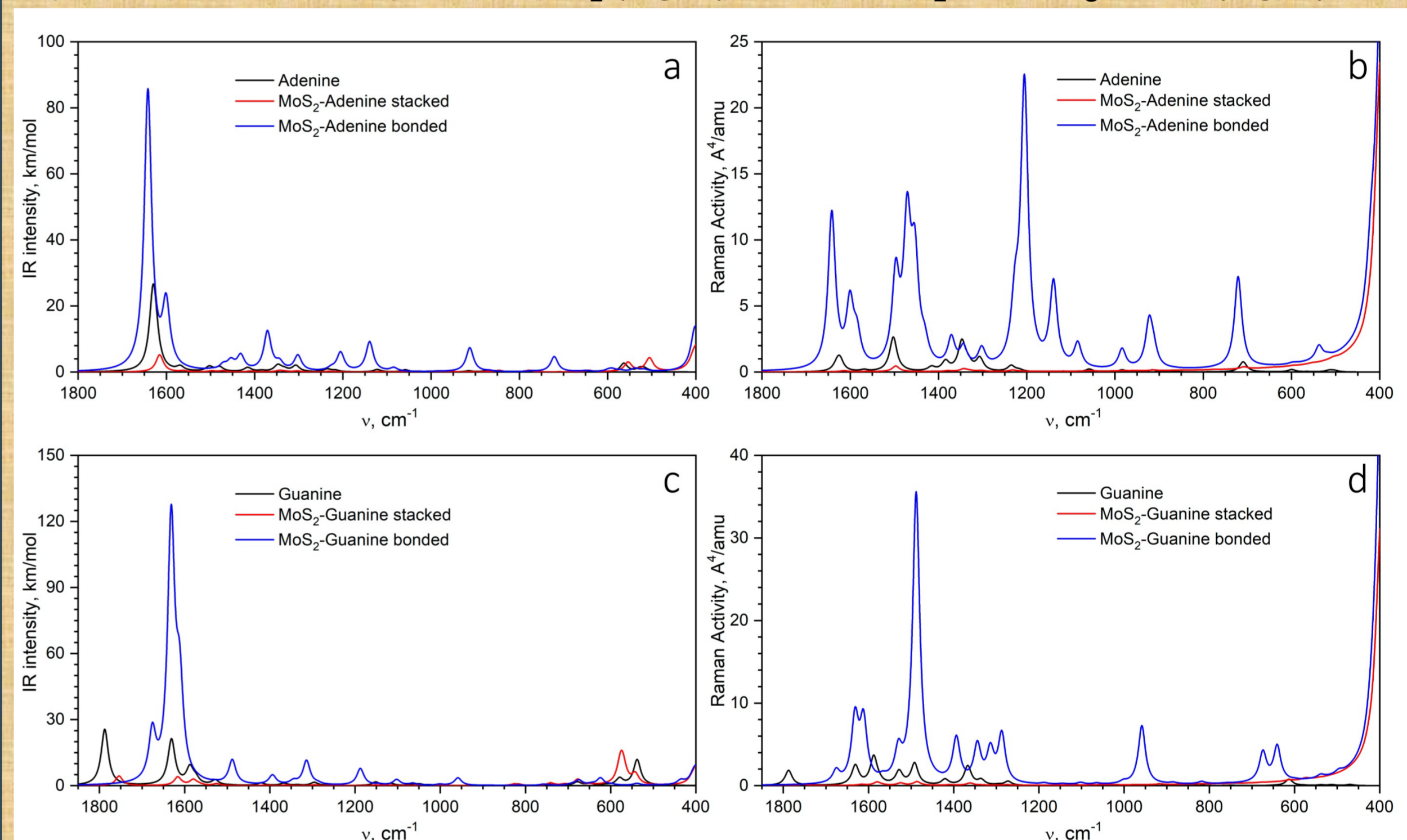


Fig. 3. Spectra of adenine and guanine complexes with pristine MoS₂.

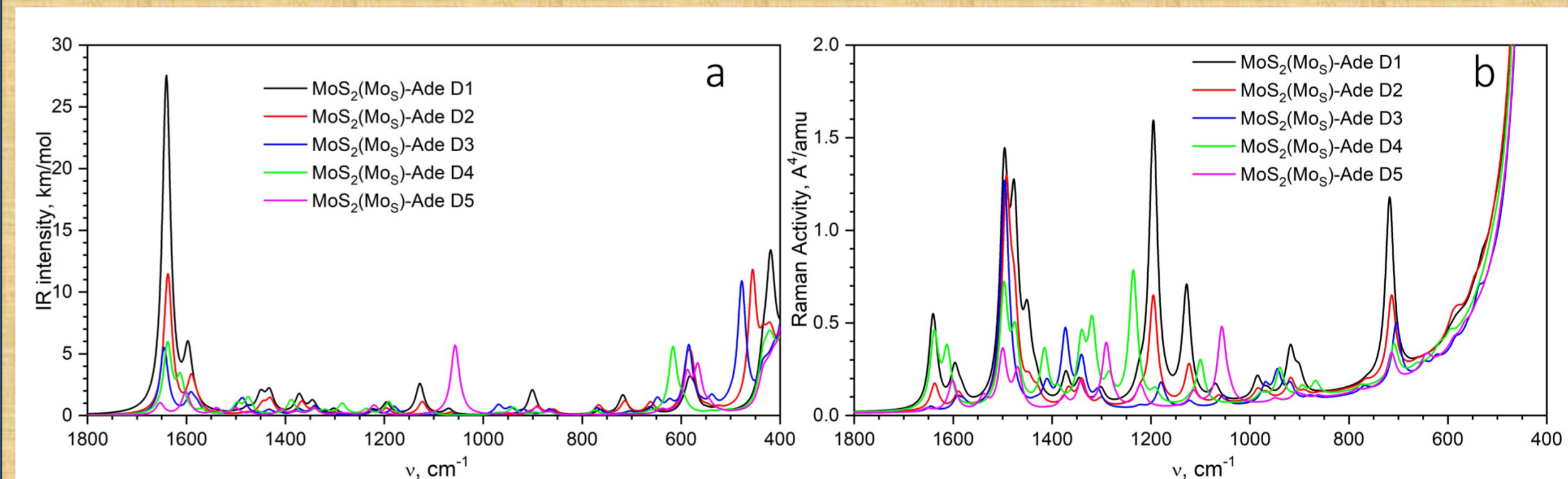


Fig. 4. Spectra of adenine with MoS₂ having the Mo_S defect.

The most significant changes in the spectra of adenine and guanine are observed for complexes with coordination bonds. The formation of the bonds with molybdenum atoms leads to significant shifts in vibrational frequencies, which amount to 100 cm⁻¹. The strongest shifts are observed for vibrations of those atoms that participate in bond formation. In addition to the shifts, a significant increase in IR intensities and Raman activities is observed for the bonded complexes. A dependence is observed between the magnitudes of spectral changes and the energies of intermolecular interactions. Thus, for guanine, the highest shift is observed for the C=O stretching vibrations in complexes with a O-Mo coordination bonds.

In the stacked complexes, changes in vibrational frequencies are significantly smaller than in the bonded ones. In the region below 2000 cm⁻¹, the maximum frequency change is 25 cm⁻¹ for the C=O stretching vibration. It should also be noted that the formation of the stacked complexes is accompanied by a significant decrease in the intensities of all vibrations both in IR and Raman spectra.