Vibrational Spectroscopy of Diimine

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1 Introduction

Diimine, the simplest azo compound, occurs in cis and trans form. We aim to compute the vibrational spectra and distinguish between the two isomers.

2 Computational Details

The structures of the diimine isomers were optimized at the TPSS level using polarized triple-ζ quality def2-TZVP basis sets. The RI-J approximation was used throughout. An analytical force constant calculation was performed to obtain normal modes, as well as their harmonic frequencies and IR intensities for the diimine isomers.

3 Results and Discussion

The work of Martin and Taylor is used as a benchmark for the geometry of diimine isomers. Table 1 contains our computed geometries for the diimine isomers [1]. For transdiimine, we obtain $r_e(NN)$, $r_e(NH)$, and θ values which deviate by -0.01%, 1.29%, and 0.18%, respectively. The cisdiimine values deviate by -0.22%, 1.44%, and 0.94%, respectively.

Computed harmonic frequencies and their IR intensities are shown in Table 2. The first 6 normal modes for all isomers have no frequency and do not contribute. Comparison of the vibrational spectra of the cis and trans isomers is available in Figure 1. Notable differences occur at $1530 - 1610 cm^{-1}$ and $2900 - 3100 cm^{-1}$, where transdiimine has no IR transmittance but cisdiimine strongly transmits.

4 Conclusion

Our computed geometries for the diimine isomers are in good agreement with the best calculation from Martin and Taylor. From the predicted vibrational spectra, we can conclude that the cis and trans diimine isomers are distinguishable.

References

[1] Jan M. L. Martin and Peter R. Taylor. "Benchmark ab initio thermochemistry of the isomers of diimine, N2H2, using accurate computed structures and anharmonic force fields". In: *Mol. Phys.* 96.4(1999), pp. 681-692.

Tables and Figures

	$r_e(NN)$	$r_e(NH)$	θ
Cis	1.2429	1.0480	112.93
Trans	1.2467	1.0414	106.36
Iso	1.2129	1.0554	124.42

Table 1: Bond lengths (Å) and bond angles (°) between the diimine isomers.

	cis		trans		iso	
	ω	Intensity	ω	Intensity	ω	Intensity
7	1263.78	0.00	1330.11	100.00	1002.69	34.25
8	1326.04	4.63	1335.60	83.08	1304.82	4.49
9	1537.72	33.65	1555.90	0.00	1582.01	17.39
10	1594.61	5.15	1611.81	0.00	1725.45	3.69
11	2966.22	100.00	3126.32	0.00	2779.13	100.00
12	3075.24	50.04	3157.10	66.21	2886.60	65.58

Table 2: Harmonic frequencies (s^{-1}) and IR intensities (%) for the normal modes of each isomer.
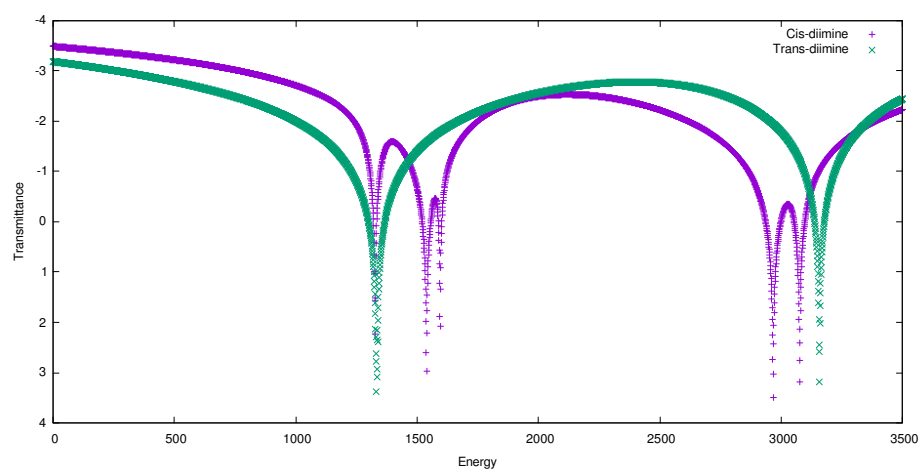
Figure 1: IR intensities of the cis and trans isomers against energy (cm^{-1}). IR intensity $(mol^{-1} \cdot cm^{-1})$ is logarithmic.