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Quantum-chemical studies of infrared spectra of ^{15}N labeled diazene isomers

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Abstract: The geometry of *trans*-HN═NH, *cis*-HN═NH and N═NH_2 containing no, one or two ^{15}N labeled atoms was optimized. The corresponding infrared vibrations were evaluated using a linear scaling factor. For each of these compounds at least one vibration can be found, which enables to distinguish between heteroisotopic $^{14}N═^{15}N$ and homoisotopic $^{14}N═^{14}N$ or $^{15}N═^{15}N$ species. Independent of the ^{15}N labeling, only *trans*-conformation should be found in the reaction mixture under equilibrium conditions.

Keywords: Coupled Cluster, isotopic labeling, geometry optimization, vibration transitions

Introduction

The reaction mechanism for homogeneous oxidation of hydrazine N_2H_4 by various oxidizing agents in aqueous solutions is more complex than in case of its heterogeneous oxidation on solid electrode surfaces (Higginson and Sutton, 1953; Cahn and Powell, 1954; Petek and Bruckenstein, 1973). Homogenous oxidation of a mixture of non-labeled ($^{14}N_2H_4$) and ^{15}N labeled ($^{15}N_2H_4$) hydrazine molecules yields $^{14}N_2$, $^{15}N^{14}N$, and $^{15}N_2$ molecules, whereas heterogeneous oxidation produces $^{14}N_2$ and $^{15}N_2$ molecules only. The formation of $^{14}N^{15}N$ molecules cannot be explained by simple removal of hydrogens from N_2H_4 molecules, the intermediate formation of N_4H_6 or N_4H_4 dimers is supposed. Quantum-chemical studies of N_4H_6 isomers in aqueous solutions at the CCSD/cc-pVTZ level of theory (Breza and Manova, 2023) explained their decomposition prevailingly into $^{15}N^{14}N$ molecules through $^{14}NH_3$...$^{14}N^{15}N$...$^{15}NH_3$ intermediates. The HN═NH and N═NH_2 species can also be formed. Due to the low stability of these species, their $^{15}N/^{14}N$ isotopic composition must be experimentally determined using sufficiently fast methods, such as infrared (IR) spectroscopy.

Early IR investigations of N_2H_2 were done by matrix isolation methods (Van Thiel and Pimentel, 1960; Milligan and Jacox, 1964; Blau and Hochheimer, 1964; Rosengreen and Pimentel, 1965; Bondybey and Nibler, 1973; Nibler and Bondybey, 1974) but the spectra were very complex due to impurities and extensive hydrogen bonding. Rather pure diazene (diimide, diamine) and significantly simplified IR spectra were obtained later (Minkwitz, 1975; Demaison et al., 1997; Craig et al., 2015). However, the correct band assignments were based on a theoretical study of Craig and Levin (Craig and Levin, 1979) (see Tab. 1). Based on high resolution IR spectroscopy of gas phase diazene, rotational constants were obtained and the structure of *trans*-diazene was confirmed (Trombetti, 1968; Carlotti et al., 1974; Hegelund et al., 1994, 1996, 1997) (see Tab. 2).

Isodiazene N═NH_2 (isodiimide, isodiimine) was obtained by photolysis of carbamoyl azide [$H_2N(CO)N_3$] and its IR spectra were also measured (Sylwester and Dervan, 1984; Teles et al., 1989) (see Tab. 1).

Quantum-chemical studies at CCSD(T) and similar levels of theory explained the energy relations among the three N_2H_2 isomers (*trans*-N_2H_2 being the most stable) and resolved the last problems of the assignment of diazene bands (Kobayashi et al., 1993; Martin and Taylor, 1999; Sekušak and Frenking, 2001; Matus et al., 2006; Spada et al., 2013) (see Tab. 2 for vibration transitions and Tab. 3 for optimal geometries and energies).

Only one old study dealing with the effect of ^{15}N labeled diazene in its experimental IR spectra was found (Rosengren and Pimentel, 1965). Triple splitting of the 1286 cm^{-1} band was observed with 1.3 and 2.6 cm^{-1} shifts for $H^{14}N═^{15}NH$ and $H^{15}N═^{15}NH$, respectively. Even larger shifts (up to 7 cm^{-1}) were predicted for another band (Craig and Levin, 1979).

The isotopic ^{15}N labeling of terminal nitrogen in $^{15}N^{14}NH_2$ lowers the 1574 cm^{-1} band to 1548 cm^{-1} (Sylwester and Dervan, 1984). Analogously, in deuterated isodiazene N═ND_2, the 1571 and 1552 cm^{-1} bands are assigned to $^{14}N═^{14}N$ and $^{14}N═^{15}N$ stretching, respectively.

The aim of our recent study was to investigate the effect of single and double ^{15}N labeling on the IR spectra of the three N_2H_2 isomers. This should enable confirmation of the above-mentioned N_2H_2 reaction intermediates (Breza and Manova, 2023) of homogenous hydrazine oxidation through dimerization because their instability can be problematic.

Tab. 1. Observed IR fundamentals (in cm^{-1}) for N_2H_2 and NNH_2 by various authors in matrices and in gas phase.

N_2H_2	N_2H_2	N_2H_2	N_2H_2	N_2H_2	N_2H_2	N_2H_2
Nibler and Bondybey, 1974	Minkwitz, 1975	Minkwitz, 1975	Demaison et al., 1997	Demaison et al., 1997	Craig et al., 2015	Craig et al., 2015
N_2 matrix IR, Raman	N_2 matrix IR	Ar matrix IR	N_2 matrix IR [b)]	Ar matrix IR [b)]	N_2 matrix IR	Ar matrix IR
1286	(1288) [a)]	(1283) [a)]	972 w	976 w	–	–
–	(1322) [a)]	(1313) [a)]	1288 vs	1283 vs	1284	1284
1529	–	–	1322 vs	1322 vs	1327	1312
1583	–	–	–	–	–	–
3128	–	3118	–	–	3131	3124
3131	3137	–	3137 w	3137 w	–	–

N_2H_2	N_2H_2	N_2H_2	NNH_2	NNH_2
Trombetti, 1971	Hallin et al., 1981	Hegelund et al., 1994	Sylwester and Dervan, 1984	Teles et al., 1989
Gas IR	Gas IR	Gas IR	Ar matrix IR	Ar matrix IR [c)]
–	–	–	1003	1002.7(1.00)
1359	1288.6386(16)	1288.64786(4)	1574	1287.5(0.008)
1404	1316.4129(15)	1316.41214(4)	1863	1574.2(0.31)
–	–	–	2141	1644.7(0.021)
3095	3120.2788(8)	3120.28676(8)	2808	2804.6(0.33)
–	–	–	2865	2862.0(0.75)

[a)]Values in parentheses are reassignments (Craig and Levin, 1979).

[b)]w – weak, vs-very strong.

[c)]relative intensities in parentheses.

Tab. 2. Calculated vibration transitions (in cm^{-1}) for N_2H_2 isomers by various authors at various levels of theory in gas phase.

Trans-HN=NH	*Trans*-HN=NH	*Cis*-HN=NH	N=NH_2	*Trans*-HN=NH	*Trans*-HN=NH
Martin and Taylor, 1997	Martin and Taylor, 1999	Martin and Taylor, 1999	Martin and Taylor, 1999	Spada et al., 2013	Spada et al., 2013
CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ aug-cc-pVTZ	CASSCF/ aug-cc-pVTZ
1294.2	1294.2	1231.9	991.0	1317	1321
1317.5	1317.4	1334.7	1292.7	1344	1354
1519.3	1528.2	1520.7	1560.4	1552	1527
1519.4	1578.5	1548.4	1665.3	1611	1617
3033.3	3051.0	2986.5	2769.7	3265	3124
3125.0	3133.3	3002.5	2866.5	3297	3158

Cis-diazene has not been detected experimentally. Isodiazene was detected shortly after formation (Sylwester and Dervan, 1984; Teles et al., 1989) probably due to its lower conversion rate.

Method

Using Gaussian16 software (Frisch et al., 2016), geometry optimization of *trans*-HN=NH, *cis*-HN=NH, and N=NH_2 with no, one or two ^{15}N labeled atoms was performed at the CCSD (Coupled Cluster using Single and Double substitutions from the Hartree-Fock determinant) level of theory (Scuseria et al., 1988) with cc-pVTZ basis sets for all atoms (Dunning, 1989). The optimized structures were tested for the absence of imaginary vibrations by vibrational analysis. Wavenumbers of vibrational transitions were multiplied by a scaling factor of 0.941 obtained from

Tab. 3. Calculated N—N, d(N—N), and N—H, d(N—H), bond lengths, N—N—H bond angles, α(N—N—H), relative energy differences, ΔE, for N_2H_2 isomers obtained at various levels of theory by various authors in gas phase.

Isomer	d(N—N) [Å]	d(N—H) [Å]	α(N—N—H) [deg]	ΔE [kJ/mol]	Method	Reference
Trans-HN=NH	1.2468	1.0281	106.17	–	CCSD(T)/cc-pVQZ	Kobayashi et al., 1993
Trans-HN=NH	1.2468	1.0281	106.17	0.00	CCSD(T)/cc-pVQZ	Martin and Taylor, 1999
Cis-HN=NH	1.2456	1.0331	111.88	21.78	CCSD(T)/cc-pVQZ	Martin and Taylor, 1999
N=NH_2	1.2172	1.0342	123.49	100.82	CCSD(T)/cc-pVQZ	Martin and Taylor, 1999
Trans-HN=NH	1.265	1.040	105.7	–	CCSD(T)/aug-cc-pVDZ	Sekušak and Frenking, 2001
Trans-HN=NH	1.2659	1.0415	105.75	–	CCSD(T)/aVDZ	Matus et al., 2006
Cis-HN=NH	1.2652	1.0464	111.57	–	CCSD(T)/aVDZ	Matus et al., 2006
Trans-HN=NH	1.2528	1.0318	106.13	0.0	CCSD(T)/aVTZ	Matus et al., 2006
Cis-HN=NH	1.2526	1.0365	111.77	21.3[a)]	CCSD(T)/aVTZ	Matus et al., 2006
Trans-HN=NH	1.247(1)	1.030(1)	106.3(1)	–	Exp.	Demaison et al., 1997

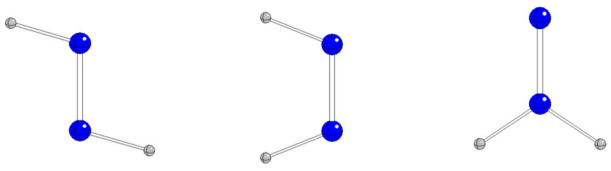
[a)]Enthalpy at 298 K

the National Institute of Standards and Technology (NIST, 2022) for CCSD/cc-pVTZ calculations.

Results and Discussion

Geometry optimization of *trans*-HN=NH, *cis*-HN=NH and N=NH_2 isomers gives stable structures of the C_{2h}, C_{2v}, and C_{2v} symmetry groups, respectively, with bond lengths and angles (see Fig. 1 and Tab. 4) very similar to previous CCSD(T)/cc-pVQZ studies (Kobayashi et al., 1993; Martin and Taylor, 1999). Single and double ^{15}N labeling causes only very small changes in structure parameters, which are lower than standard numerical accuracy. Gibbs energy data indicate the highest stability of *trans*-HN=NH, independent of ^{15}N labeling (Tab. 5), in agreement with analogous energy data from (Martin and Taylor, 1999; Matus et al., 2006), suggesting that only *trans*-HN=NH can be found in the reaction system under equilibrium conditions.

IR vibrational transitions calculated in previous studies (Martin and Taylor, 1997, 1999; Spada et al., 2013) do not include scaling factors. Their values are usually overestimated, although sometimes very exact. To improve the results, linear scaling factors for the CCSD method and cc-pVTZ basis sets (NIST, 2022) were applied to multiply the calculated wavenumbers of vibrational transitions.



Trans-diazene *Cis*-diazene Isodiazene

Fig. 1. CCSD/cc-pVTZ optimized structures of studied compounds (N — blue, H — gray).

Trans-diazene (C_{2h} symmetry group) has three IR active vibrations (one of a_u and two of b_u symmetries), the remaining three vibrations of a_g symmetry are active only in Raman spectroscopy (Tab. 6). Unlike other studies (Martin and Taylor, 1997, 1999; Spada et al., 2013), our data for the non-labeled compound are underestimated, and their deviations from the most exact experimental data (Hallin et al., 1981; Hegelund et al., 1994) are higher. The two most intense (the two lowest) transitions exhibit up to 2 cm^{-1} shifts of *trans*-H^{15}N=^{14}NH related to those of other isotopic composition. Its highest b_u vibration, despite having lower intensity, exhibits analogous shifts of –6 and +4 cm^{-1} related to homoisotopic compounds.

Cis-diazene (C_{2v} symmetry) has three a_1, one a_2, and two b_1 vibrations which can be IR active (Tab. 7). There are no experimental data for this isomer. The most intense b_1 vibration of *cis*-H^{15}N=^{14}NH exhibits –8 and +5 cm^{-1} shifts related to its homoisotopic counterparts. The other two intense vibrations also exhibit lower but measurable shifts.

Isodiazene (C_{2v} symmetry) has three a_1, two b_1, and one b_2 IR active vibrations (Tab. 8). Its three most intense transitions exhibit only negligible differences between their homoisotopic and heteroisotopic counterparts. Only the a_1 vibration of medium intensity is split four times. It contains two heteroisotopic bands separated by 6 cm^{-1} and two homoisotopic bands shifted from their center by +20 and –20 cm^{-1}.

Tab. 4. Bond lengths and angles of optimized geometries of compounds under study.

	Trans-HN═NH	*Cis*-HN═NH	N═NH_2
Bond lengths [Å]			
N—N	1.243	1.242	1.217
N—H	1.028	1.033	1.032
Bond angles [deg]			
N—N—H	106.1	111.9	123.6
H—N—H	–	–	112.9

Tab. 5. Absolute, G_{298}, and relative, ΔG_{298}, Gibbs energies at 298 K of studied systems (related to *trans*-isomer of the same isotopic composition).

	G_{298} [Hartree]	ΔG_{298} [kJ/mol]
Trans-$H^{14}N{=}^{14}NH$	–110.45183	0.00
Cis-$H^{14}N{=}^{14}NH$	–110.44397	20.64
$^{14}N{=}^{14}NH_2$	–110.41327	101.24
Trans-$H^{15}N{=}^{15}NH$	–110.45218	0.00
Cis-$H^{15}N{=}^{15}NH$	–110.44366	22.37
$^{15}N{=}^{15}NH_2$	–110.41361	101.27
Trans-$H^{15}N{=}^{14}NH$	–110.45201	0.00
Cis-$H^{15}N{=}^{14}NH$	–110.44349	22.37
$^{15}N{=}^{14}NH_2$	–110.41342	101.32
$^{14}N{=}^{15}NH_2$	–110.41346	101.21

Tab. 6. Symmetries, Γ (within the C_{2h} group), calculated wavenumbers, ν, and IR intensities, I, of vibration transitions of *trans*-diazenes of various $^{14}N/^{15}N$ isotopic composition. Most suitable transition for *trans*-$H^{15}N{=}^{14}NH$ determination is highlighted in bold.

Γ	*Trans*-$H^{14}N{=}^{14}NH$		*Trans*-$H^{15}N{=}^{15}NH$		*Trans*-$H^{15}N{=}^{14}NH$	
	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]
a_u	1273.1	94.5	1270.9	94.0	1272.3	94.3
b_u	1286.0	93.2	1283.8	92.7	1285.1	92.9
a_g	1526.4	0.0	1484.6	0.0	1508.3	0.0
a_g	1551.3	0.0	1531.9	0.0	1539.4	0.0
a_g	3118.4	0.0	3108.7	0.0	3111.6	0.3
b_u	3147.2	18.5	3137.1	18.6	**3141.1**	18.3

Tab. 7. Symmetries, Γ (within the C_{2v} group), calculated wavenumbers, ν, and IR intensities, I, of vibration transitions of *cis*-diazenes of various $^{14}N/^{15}N$ isotopic composition. Most suitable transition for *cis*-$H^{15}N{=}^{14}NH$ determination is highlighted in bold.

Γ	*Cis*-$H^{14}N{=}^{14}NH$		*Cis*-$H^{15}N{=}^{15}NH$		*Cis*-$H^{15}N{=}^{14}NH$	
	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]
a_2	1209.9	0.0	1203.0	0.0	1206.2	0.0
a_1	1312.2	0.6	1309.5	0.7	1310.5	0.7
b_1	1491.9	66.9	1478.9	68.0	**1484.4**	66.0
a_1	1549.3	2.9	1498.4	2.6	1524.5	4.2
b_1	3005.5	53.5	3000.8	53.2	3004.0	53.3
a_1	3087.5	30.6	3082.3	30.2	3085.9	30.4

Tab. 8. Symmetries, Γ (within C_{2v} group), calculated wavenumbers, ν, and IR intensities, I, of vibration transitions of isodiazenes of various $^{14}N/^{15}N$ isotopic composition. Most suitable transitions for $^{15}N{=}^{14}NH_2$ determination are highlighted in bold.

Γ	$^{14}N{=}^{14}NH_2$		$^{15}N{=}^{15}NH_2$		$^{15}N{=}^{14}NH_2$		$^{14}N{=}^{15}NH_2$	
	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]	ν [cm^{-1}]	I [km/mol]
b_2	946.5	109.5	938.4	111.0	945.8	110.3	939.2	110.2
b_1	1264.0	2.7	1253.8	3.2	1260.8	2.9	1257.0	2.9
a_1	1527.5	13.3	1479.3	12.5	**1500.4**	12.8	**1506.9**	13.1
a_1	1647.5	0.0	1641.2	0.0	1647.4	0.0	1641.2	0.0
a_1	2995.2	64.5	2993.1	64.1	2995.0	64.7	2993.4	64.0
b_1	3009.1	56.4	2999.2	55.3	3009.1	56.4	2999.2	55.3

Finally, it can be concluded that heteroisotopic diazenes (*trans*-$H^{15}N{=}^{14}NH$ and *cis*-$H^{15}N{=}^{14}NH$) and isodiazenes ($^{15}N{=}^{14}NH_2$ and $^{14}N{=}^{15}NH_2$) can be detected by IR measurements. Another problem is finding suitable scaling factors for (iso)diazenes. It seems that linear scaling factors are insufficient for accurate calculation of IR active vibrations. More complex solutions to this problem should be proposed in future research.

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