Vibrational Bands of $H_xN_yO_z$ Molecules

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A compilation of experimental data is presented which covers all known molecular species fitting the $^1H_x{}^{14}N_y{}^{16}O_z$ ($y, z \neq 0$) chemical formula. The vibrational bands of these compounds in gas, liquid, solid, and matrix are listed together with their assignments and the relevant references. Most of the literature before October 1991 is covered.

Key words: atmospheric data; combination bands; fundamental bands; fundamental frequencies; infrared spectra; nitrogen acids; nitrogen oxides; overtone bands; polyatomic molecules; Raman spectra; vibration-rotation spectra; spectroscopic tables.

Contents

1. Introduction

As pointed out by L. Pauling[1] in his book on "The Nature of the Chemical Bond," nitric oxide (NO) is the most stable of the odd molecules. This notion of oddness, introduced by Lewis[2] in 1916, refers to the total number of electrons in the molecule. The notion of triple electron bond was introduced to explain the stability of such species. As a consequence, the latter were not expected to polymerize. It is nowadays established that NO–NO Van der Waals type bondings can be formed, under appropriate experimental conditions, thus somewhat in contradiction with that earlier statement. This holds even more firmly for the next member of this NO_z family, nitrogen dioxide (NO_2), known for a long time to be in thermodynamic equilibrium with the dimer N_2O_4. The geometrical structure of the dimer species is planar, but the various bond lengths and angles remain to be accurately determined. There is even a more basic structural problem about the next member of the family, nitrogen trioxide (NO_3). Although it appears likely that the molecule is planar in its ground electronic state, it is not obvious whether the three N–O bonds are identical. The existence of the corresponding dimer (N_2O_6) is not even reported in the literature.

Even species of nitrogen and oxygen (N_yO_z, $y = 2,4,...$) are also known to exist. The simplest one, nitrous oxide (N_2O), has been extensively studied and its stable linear geometry demonstrated. N_2O_2, N_2O_4 (already mentioned), N_2O_3, and N_2O_5 have been observed, but their structural and chemical properties remain to be well characterized. One can even postulate the existence of other larger species fitting the chemical formula N_yO_z.

In the presence of water (H_2O), the N_yO_z species react with each other and form an extensive system with many chemical interplays. Indeed, several chemical equilibria take place, resulting into the formation of new, although connected species, such as nitrous acid (HONO) or nitric acid (HNO_3). Examples of these reactions are as follows:

$$NO + NO_2 + H_2O \leftrightarrow 2HONO$$
$$HONO_{cis} \leftrightarrow HONO_{trans}$$
$$NO + NO_2 \leftrightarrow N_2O_3$$
$$2NO_2 \leftrightarrow N_2O_4$$
$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO$$
$$NO_2 + NO_3 \leftrightarrow N_2O_5$$

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Most of the above reactions are such that the species coexist each in reasonable abundance under a wide range of experimental conditions. This is certainly the case in the terrestrial atmosphere, and thus in any laboratory experiment performed under similar temperature and pressure conditions. It turns out that the role of the $H_xN_yO_z$ species is central in various master physico-chemical processes occurring in our atmosphere. One can refer for instance to the balance of ozone (O_3), or to the formation of acid rain, two of the atmospheric cycles in which some of the $H_xN_yO_z$ species directly participate, as described in the book of Finlayson-Pitts and Pitts, Jr.[3] Because of the internal chemical connections we have mentioned, all members of the family are indirectly contributing. Thus the study of that chemical family as a whole is meaningful. It is actually of fundamental importance not only in the environmental context, but also in various other up to date chemical areas, such as those dealing with combustion, energy transfers or chemical bondings.

The basic role of infrared spectroscopy in probing the $H_xN_yO_z$ molecules is well established, in particular in the atmospheric area. As a consequence of the trends we have pointed out, several of the family members are usually present in most realistic situations. Any related infrared spectrum will thus demonstrate the presence of various species through an extended series of bands. The bands will strongly overlap, not only because of their high density, but also because the probed molecules are very similar, and thus present very close vibrational frequencies. It appears critical to be able to fully assign such data in order to achieve an optimal diagnosis of the monitored sample *in situ* or in the laboratory. An exhaustive knowledge of the infrared spectrum of each individual species is therefore required. Of course, it is well known that spectral information recorded with high resolution will allow us in most cases to bypass this general prospect, and to immediately focus on some specific properties. However, such type of data are available for the lightest species only, and furthermore restricted to gas phase investigations.

The interest for a database collecting all the infrared spectral information appears consequently justified for many applications in atmospheric, fundamental, or analytical chemistry. It is the aim of the present compilation to provide such comprehensive and coherent information, at the stage of the literature existing nowadays.

The review by Laane and Ohlsen[4] provides interesting and complete background information on the role of the $H_xN_yO_z$ molecules in various areas. Some spectroscopic infrared data are given in that earlier review. A more complete database has since been published by Jacox[5], and compilations aimed at the investigation of the atmosphere are now also available [e.g., GEISA (Husson *et al.*[6]), HITRAN (Rothman *et al.*[7]), ATMOS (Brown *et al.*[8])], which all are oriented towards infrared spectroscopy. In all cases, however, the spectroscopic content remains quite incomplete as only some of the species we are interested in are concerned, or only the fundamental frequencies are collected, or a very limited number of vibrational bands is provided. These previous works unfortunately do not really save the effort of a time consuming bibliographic research to produce exhaustive information on the vibrational bands of the members of the $H_xN_yO_z$ chemical family, as we have actually experienced ourselves during our current research work.

Our present compilation is, in a way, an updating and an extension of the various tables provided in the book on infrared and Raman spectroscopy by Herzberg[9] (1st edition in 1949, new edition in preparation), which systematically lists some of the observed vibrational bands. We hope that the present tables will help scientists from different fields in their investigation on the $H_xN_yO_z$ family of molecules, which we believe to be of central importance in chemistry.

2. Scope of Review and Guide to the Compilation

We have considered the various known neutral species fitting the $H_xN_yO_z$ chemical formula, taking into account the main isotopic species only, i.e., ^1H,^{14}N, and ^{16}O. Their vibrational bands constitute the main information we have compiled. The energy range considered extends from the far infrared towards the near infrared, depending on the scientific publications on each species. Data from all phases are taken into account. The spectral information is presented in various forms in sets of tables. Each set concerns a different species. They are all built in a similar way. The first table in a set provides, for each known or postulated molecular geometry, the molecular point group, the symmetry and labeling of the corresponding normal modes of vibration, and their Raman and infrared activities. The labeling is the most conventional one usually reported in the various literature investigations. For each of the classes of isomeric forms of the species, the various modes of vibration are then briefly characterized in a second table in terms of the corresponding motions of the nuclei, and of their observed frequencies. The observed vibrational bands are listed in a final table.

The table of *fundamental* vibrational frequencies takes into account all wavenumbers found in the literature. Each of the listed frequencies, for each mode, usually corresponds, however, to a mean value whenever several literature data agree with each other within 5 cm^{-1}. All the various references are mentioned, with appropriate remarks concerning the experimental medium used in the study. In some cases however, one of the values was preferred because it is the result of more accurate gas phase experiments. The corresponding work is then underlined in the list of references.

In the table collecting the *observed* vibrational bands, only one of the frequencies reported in the literature is given. Again, it corresponds to the gas phase result, when available. Otherwise, the selection is based on other criteria which are not detailed. The experiments reported in the literature are of various types, and, as already pointed out, may concern quite different media. The overall resolution and accuracy is thus highly variable from one wavenumber to another in the table. In any case the remarks in the appropriate column in the table present the main characteristics of the related experiment. As a general rule, the wavenumbers correspond to the band origin, when arising from gas phase or matrix experiments. We also included the values for the R, Q, or P head measurements, when available in the literature. The band type is specified whenever it is detailed in the publications.

As already pointed out, the most accurate data arise from gas phase experiments; however, investigations on liquids may provide more complete information because of the stronger intensity of the bands, especially for those observed only through the Raman effect, while experiments performed in matrices are usually dedicated to the characterisation of less stable isomeric forms. The various wavenumbers may arise from totally different experimental techniques and the reader is referred to the original papers mentioned for further details.

We have noted in the tables whenever a list of rovibrational wavenumbers for a specified band appears in the atmospheric databases HITRAN (Rothman *et al.*[7]) and/or ATMOS (Brown *et al.*[8]). One should be aware that such a list usually corresponds to calculated wavenumbers. It also often happens that the corresponding measured wavenumbers are either directly provided or made available on request by the authors of the original paper, to which we always refer.

3. Units and Abbreviations

The usual spectroscopic unit for the wavenumber (cm^{-1}) is used to characterize the spectral observations.

The following abbreviations are used throughout the tables:

Vibration type:

s-	symmetric
a-	asymmetric

Activity:

A	active band
I	inactive band

Experimental spectroscopic technique:

DL	Diode Laser
E	Infrared Emission (conventional or Fourier Transform Spectroscopy)
H	Heterodyne Frequency Measurements
IR	Infrared Absorption (conventional or Fourier Transform Spectroscopy)
LIF	Laser Induced Fluorescence
LMR	Laser Magnetic Resonance
LSS	Laser Stark Spectroscopy
MW	Microwave Spectroscopy
Ra	Raman Spectroscopy

Medium:

G	Gas
L	Liquid
LXe	Liquid Xenon
M	Matrix (see the referred paper for more details)
M:x,y	Matrix (medium specified as x,y,...; e.g., Ar, Ne, Xe, N_2...)
S	Solid

Band type:

(a,B)-	hybrid band; rotational envelope with some dominant B-type character
(A,b)-	hybrid band; rotational envelope with some dominant A-type character
(A,B)-	hybrid band; rotational envelope with evenly mixed A- and B-type character

4. Tables

4.1. NO

Molecular Constants

	Vibrational constants (cm^{-1})[a]	Spin-orbit constants (cm^{-1})[b]	References, Remarks
Y_0	−948.5465(14)	123.25241(63)	[c,d]
Y_1	1904.1346(18)	−0.23570(48)	6,7(E,G)
Y_2	−14.08836(89)	−0.00408(10)	
$Y_3 \times 10^{+2}$	1.005(20)	−0.01863(74)	
$Y_4 \times 10^{+4}$	−1.53(22)		
$Y_5 \times 10^{+6}$	−9.8(1.4)	−0.252(18)	
$Y_6 \times 10^{+7}$	−1.91(43)	−0.0239(47)	
$Y_7 \times 10^{+9}$	−5.27(53)		
$\Delta G_{1/2}$	1875.98918(3)		[c,d] 3,4(IR,G); 10(H,G) See also 8,9 and references therein

[a] For $v \leqslant 22$, the vibrational level energies are expressed in terms of Dunham coefficients as following:

$$G(v) = \sum_{i=0} Y_i \, (v + 1/2)^i.$$

[b] For $v \leqslant 22$, the energy separation between $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ is roughly expressed in terms of Dunham coefficients as following:

$$A(v) = \sum_{i=0} Y_i \, (v + 1/2)^i.$$

[c] Number in parentheses refers to the last quoted digits and represents one standard deviation.

[d] For other results or more details, see also Huber and Herzberg's tables[5].

Observed Infrared Bands

Frequency (cm^{-1})	Assignment v'	v''	Transition	References	Remarks
1763.8766	5	4		8,9	[a]
1791.8403	4	3		8,9	[a]
1819.8392	3	2		8,9	[a]
1847.8808	2	1		8,9	[a]
1875.8804	1	0	$\Pi_{3/2} - \Pi_{3/2}$	3(IR,G)	Sub-band origin
1875.98918(3)	1	0		10(H,G)	[b,c,d] See also 3,4(IR,G)
1876.0897	1	0	$\Pi_{1/2} - \Pi_{1/2}$	3(IR,G)	Sub-band origin
1995.5917			$\Pi_{3/2} - \Pi_{1/2}$		
2993.5237	15	13		7(E,G)	[e]
3050.6806	14	12		7(E,G)	[e]
3107.4567	13	11		7(E,G)	[e]
3163.9320	12	10		7(E,G)	[e]
3220.1770	11	9		7(E,G)	[e]
3276.2541	10	8		7(E,G)	[e]
3332.2163	9	7		7(E,G)	[e]
3388.1105	8	6		7(E,G)	[e]
3443.9758	7	5		7(E,G)	[e]
3499.8472	6	4		7(E,G)	[b,c,e]
3555.7523	5	3		7(E,G)	[b,c,e]
3570.4331 R_2	6	4	$\Pi_{3/2} - \Pi_{3/2}$	6(E,G)	
3570.8048 R_1			$\Pi_{1/2} - \Pi_{1/2}$		
3611.7150	4	2		7(E,G)	[b,c,e] See also 1(E,G)
3667.7552	3	1		7(E,G)	[b,c,e] See also 1(E,G)

Observed Infrared Bands — Continued

Frequency (cm^{-1})		Assignment			References	Remarks
		v'	v''	Transition		
3685.7860	R_2	4	2	$\Pi_{3/2} - \Pi_{3/2}$	6(E,G)	See also 1(E, G)
3686.1018	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
3723.85233(13)		2	0		4(IR,G)	[b,c,d] See also 1,6,7(E,G); 2(IR,G)
3743.5741	R_2	3	1	$\Pi_{3/2} - \Pi_{3/2}$	6(E,G)	See also 1(E,G)
3743.8708	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
3801.4564	R_2	2	0	$\Pi_{3/2} - \Pi_{3/2}$	6(E,G)	See also 1(E,G)
3801.7282	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
3907.2464	ν_0	22	19		7(E,G)	[e]
3933.996	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
3936.548	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4001.0060	ν_0	21	18		7(E,G)	[e]
4029.361	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4031.631	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4092.9246	ν_0	20	17		7(E,G)	[e]
4122.836	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4124.881	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4183.2654	ν_0	19	16		7(E,G)	[e]
4214.668	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4216.527	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4272.2556	ν_0	18	15		7(E,G)	[e]
4305.126	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4306.792	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4360.1038	ν_0	17	14		7(E,G)	[e]
4394.402	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4395.907	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4446.9970	ν_0	16	13		7(E,G)	[e]
4482.661	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4484.049	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4533.0999	ν_0	15	12		7(E,G)	[e]
4570.134	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4571.364	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4618.5611	ν_0	14	11		7(E,G)	[e]
4656.894	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4658.046	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4703.5082	ν_0	13	10		7(E,G)	[e]
4743.146	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4744.176	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4788.0575	ν_0	12	9		7(E.G)	[e]
4828.949	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4829.919	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4872.3056	ν_0	11	8		7(E,G)	[e]
4914.460	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
4915.329	R_1			$\Pi_{1/2} - \Pi_{1/2}$		
4956.3418	ν_0	10	7		7(E,G)	[e]
4999.717	R_2			$\Pi_{3/2} - \Pi_{3/2}$		
5000.540	R_1			$\Pi_{1/2} - \Pi_{1/2}$		

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment v'	v''	Transition	References	Remarks
5170.8 R_1	8	5	$\Pi_{1/2} - \Pi_{1/2}$	1(E,G)	
5255.4 R_1	7	4	$\Pi_{1/2} - \Pi_{1/2}$	1(E,G)	
5340.1 R_1	6	3	$\Pi_{1/2} - \Pi_{1/2}$	1(E,G)	
5425.5 R_1	5	2	$\Pi_{1/2} - \Pi_{1/2}$	1(E,G)	
5511.0 R_1	4	1	$\Pi_{1/2} - \Pi_{1/2}$	1(E,G)	
5543.69160(19)	3	0		4(IR,G)	[d]See also 2(IR,G)
5595.1 R_1	3	0		1(E,G)	
7335.158	4	0	$\Pi_{3/2} - \Pi_{3/2}$	2(IR,G)	Sub-band origins
7336.031			$\Pi_{1/2} - \Pi_{1/2}$		
~9100 ν_0	5	0		11(IR,G)	
~9130 R					

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[a] Band origin; line positions calculated with the parameters obtained by 6(E,G).

[b] Rotational line list available in HITRAN database (8).

[c] Rotational line list available in ATMOS database (9).

[d] Band origin calculated from rotational analysis; the number in parentheses refers to the last quoted digits and represents one standard deviation.

[e] Band origin calculated from $G(v)$ values: these latter vibrational energy values were obtained from a simultaneous least-squares fitting of the rovibrational data in the 1–0, 2–1, $\Delta v = 2$, and $\Delta v = 3$ bands [see 6,7(E,G) for more details].

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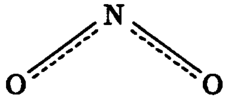
4.2. NO_2

Species	Molecular point group	Normal modes Symmetry	Normal modes Vibrations	Activity Raman	Activity Infrared
	C_{2v}	A_1 B_2	ν_1, ν_2 ν_3	A A	A A

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1	ν_1	s-stretch	1319.770	3,24(LIF,G); 6(Ra,G); 13(Ra,M:Ar,Kr,Xe); 15,$\underline{17}$(IR,G)
	ν_2	bend	749.6530	3,24(LIF,G); 4,5,15,$\underline{23}$(IR,G); 6(Ra,G); 13(Ra,M:Ar,Kr,Xe); 14(LMR,G)
B_2	ν_3	a-stretch	1616.85	3,24(LIF,G); 9,$\underline{15}$(IR,G); 13(Ra,M:Ar,Kr,Xe)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
749.652961(29)	ν_2^0 *B*-type band	23(IR,G)	[a,b]($\nu_1,2\nu_2,\nu_3$)+($\nu_2+\nu_3,3\nu_2$), [c,d] See also 3,24(LIF,G); 4,5,15(IR,G); 6(Ra,G); 13(Ra,M); 14(LMR,G)
1319.77065(34)	ν_1^0 *B*-type band	17(IR,G)	[a,b]($\nu_1,2\nu_2,\nu_3$) See also 3,24(LIF,G); 6(Ra,G); 13(Ra,M); 15(IR,G)
1498.3474(16)	$2\nu_2^0$	18(IR,G)	[a,b]($\nu_1,2\nu_2,\nu_3$),[d] See also 6(Ra,G); 9,15(IR,G); 13(Ra,M); 24(LIF,G)
1605.497	$\nu_3+\nu_2-\nu_2$ *A*-type band	15(IR,G)	[d] Calculation from ($\nu_2+\nu_3$) and ν_2 frequencies
1616.8535(20)	ν_3^0 *A*-type band	15(IR,G)	[a,b]($\nu_1,2\nu_2,\nu_3$)+($\nu_2+\nu_3,3\nu_2$), [c,d] See also 3,24(LIF,G); 9(IR,G); 13(Ra,M)
2063.11761(29)	$(\nu_1+\nu_2)^0$ *B*-type band	20(IR,G)	[a] See also 6(Ra,G); 13(Ra,M); 24(LIF,G)
2245.991(20)	$3\nu_2^0$	15(IR,G)	[a,b]($3\nu_2,\nu_2+\nu_3$) See also 9(IR,G); 13(Ra,M); 24(LIF,G)
2355.1510(20)	$(\nu_2+\nu_3)^0$ *A*-type band	15(IR,G)	[a,b]($3\nu_2,\nu_2+\nu_3$) See also 9(IR,G); 24(LIF,G)

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
2627.3370(17)	$2v_1^0$ *B*-type band	5(IR,G)	[a] See also 6(Ra,G); 13(Ra,M); 24(LIF,G) Anomalies could be due to Coriolis interaction with v_1+v_3
2805.512(17)	$(v_1+2v_2)^0$	12(IR,G)	[a,b](v_1+v_3,v_1+2v_2),[c,d] See also 6(Ra,G); 13(Ra,M); 24(LIF,G)
2898.1930	$v_1+v_3+v_2-v_2$	21,22	Calculated line positions See also 12(IR,G)
2906.0697(2)	$(v_1+v_3)^0$ *A*-type band	12(IR,G)	[a,b](v_1+v_3,v_1+2v_2),[c,d] See also 24(LIF,G)
2993.060	$4v_2^0$	9(IR,G)	See also 13(Ra,M); 24(LIF,G)
3092.48082(50)	$(2v_2+v_3)^0$ *A*-type band	9(IR,G)	[a,b]$(2v_2+v_3,2v_3)$ See also 24(LIF,G)
3201.44395(39)	$2v_3^0$ *B*-type band	9(IR,G)	[a,b]$(2v_2+v_3,2v_3)$ See also 6(Ra,G); 13(Ra,M); 24(LIF,G)
3364.57	$(2v_1+v_2)^0$	24(LIF,G)	[e] See also 6(Ra,G); 13(Ra,M)
3546.887(36)	$(v_1+3v_2)^0$	12(IR,G)	[a,b]$(v_1+3v_2,v_1+v_2+v_3)$ See also 6(Ra,G); 9(IR,G); 13(Ra,M); 24(LIF,G)
3637.84747(47)	$(v_1+v_2+v_3)^0$ *A*-type band	9(IR,G)	[a,b]$(v_1+3v_2,v_1+v_2+v_3)$ See also 12(IR,G); 13(Ra,M); 16(LMR,G); 24(LIF,G)
3738.6	$5v_2^0$	3(LIF,G)	See also 13(Ra,M); 24(LIF,G)
3829.34	$(3v_2+v_3)^0$	24(LIF,G)	[e]
3922.61	$3v_1^0$	24(LIF,G)	[e] See also 6(Ra,G); 13(Ra,M)
3929.12	$(v_2+2v_3)^0$	24(LIF,G)	[e] See also 6(Ra,G); 13(Ra,M)
4100.150(18)	$(2v_1+2v_2)^0$	19(IR,G)	[a,b]$(2v_1+2v_2,2v_1+v_3)$ See also 6(Ra,G); 13(Ra,M); 24(LIF,G)
4179.9416(34)	$(2v_1+v_3)^0$	19(IR,G)	[a,b]$(2v_1+2v_2,2v_1+v_3)$ See also 24(LIF,G)
4286.82	$(v_1+4v_2)^0$	24(LIF,G)	[e] See also 6(Ra,G); 13(Ra,M)
4369.10	$(v_1+2v_2+v_3)^0$	24(LIF,G)	[e]
4461.07	$(v_1+2v_3)^0$	24(LIF,G)	[e] See also 6(Ra,G); 13(Ra,M)
4482.57	$6v_2^0$	24(LIF,G)	[e] See also 13(Ra,M)
4564.22	$(4v_2+v_3)^0$	24(LIF,G)	[e]

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
4652.00	$(3v_1+v_2)^0$	24(LIF,G)	^{c}
4655.04(13)	$(2v_2+2v_3)^0$	19(IR,G)	$^{a,b}(2v_2+2v_3,3v_3)$ See also 6(Ra,G); 13(Ra,M); 24(LIF,G)
4754.20760(31)	$3v_3^0$ *A*-type band	19(IR,G)	$^{a,b}(2v_2+2v_3,3v_3)$ See also 1(IR,G); 24(LIF,G)
4835.05	$(2v_1+3v_2)^0$	24(LIF,G)	^{c} See also 6(Ra,G); 13(Ra,M)
4905.52	$(2v_1+v_2+v_3)^0$	24(LIF,G)	^{c}
5025.20	$(v_1+5v_2)^0$	24(LIF,G)	^{c} See also 13(Ra,M)
5098.00	$(v_1+3v_2+v_3)^0$	24(LIF,G)	^{c}
5180.54	$(v_1+v_2+2v_3)^0$	24(LIF,G)	^{c} See also 6(Ra,G); 13(Ra,M)
5205.81	$4v_1^0$	24(LIF,G)	^{c} See also 6(Ra,G); 13(Ra,M)
5224.55	$7v_2^0$	24(LIF,G)	^{c}
5298.16	$(5v_2+v_3)^0$	24(LIF,G)	^{c}
5377.91	$(3v_2+2v_3)^0$	24(LIF,G)	^{c}
5384.41	$(3v_1+2v_2)^0$	24(LIF,G)	^{c} See also 6(Ra,G); 13(Ra,M)
5437.540(12)	$(3v_1+v_3)^0$ *A*-type band	2(IR,G)	^{a} See also 24(LIF,G)
5469.66	$(v_2+3v_3)^0$	24(LIF,G)	^{c}
5568.41	$(2v_1+4v_2)^0$	24(LIF,G)	^{c} See also 13(Ra,M)
5630.36	$(2v_1+2v_2+v_3)^0$	24(LIF,G)	^{c}
5701.41	$(2v_1+2v_3)^0$	24(LIF,G)	^{c} See also 6(Ra,G)
5762.23	$(v_1+6v_2)^0$	24(LIF,G)	^{c} See also 6(Ra,G); 13(Ra,M)
5826.29	$(v_1+4v_2+v_3)^0$	24(LIF,G)	^{c}
5898.94	$(v_1+2v_2+2v_3)^0$	24(LIF,G)	^{c} See also 6(Ra,G)
5930.66	$(4v_1+v_2)^0$	24(LIF,G)	^{c} See also 6(Ra,G)
5965.61	$8v_2^0$	24(LIF,G)	^{c}
5984.705(4)	$(v_1+3v_3)^0$ *A*-type band	1(IR,G)	^{a} See also 24(LIF,G)
6030.71	$(6v_2+v_3)^0$	24(LIF,G)	^{c}

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
6101.80	$(4v_2+2v_3)^0$	24(LIF,G)	[e]
6112.11	$(3v_1+3v_2)^0$	24(LIF,G)	[e] See also 6(Ra,G)
6156.25	$(3v_1+v_2+v_3)^0$	24(LIF,G)	[e]
6183.61	$(2v_2+3v_3)^0$		
6275.98	$4v_3^0$		
6299.70	$(2v_1+5v_2)^0$		
6351.40	$(2v_1+3v_2+v_3)^0$		
6414.16	$(2v_1+v_2+2v_3)^0$		
6475.05	$5v_1^0$	24(LIF,G)	[e] See also 6(Ra,G)
6497.60	$(v_1+7v_2)^0$	24(LIF,G)	[e]
6552.84	$(v_1+5v_2+v_3)^0$		
6616.53	$(v_1+3v_2+2v_3)^0$		
6653.54	$(4v_1+2v_2)^0$		
6676.86	$(4v_1+v_3)^0$		
6693.12	$(v_1+v_2+3v_3)^0$		
6705.23	$9v_2^0$		
6761.44	$(7v_2+v_3)^0$		
6823.80	$(5v_2+2v_3)^0$		
6837.75	$(3v_1+4v_2)^0$		
6872.10	$(3v_1+2v_2+v_3)^0$		
6897.37	$(3v_2+3v_3)^0$		
6921.67	$(3v_1+2v_3)^0$		
6979.21	$(v_2+4v_3)^0$		
7029.48	$(2v_1+6v_2)^0$		
7072.23	$(2v_1+4v_2+v_3)^0$		
7125.60	$(2v_1+2v_2+2v_3)^0$		
7192.29	$(2v_1+3v_3)^0$		
7193.35	$(5v_1+v_2)^0$		
7231.06	$(v_1+8v_2)^0$		
7277.83	$(v_1+6v_2+v_3)^0$		
7332.45	$(v_1+4v_2+2v_3)^0$		
7374.57	$(4v_1+3v_2)^0$		
7386.33	$(4v_1+v_2+v_3)^0$		
7403.04	$(v_1+2v_2+3v_3)^0$		
7443.09	$10v_2^0$		
7478.02	$(v_1+4v_3)^0$		
7492.23	$(8v_2+v_3)^0$		
7544.62	$(6v_2+2v_3)^0$		
7562.47	$(3v_1+5v_2)^0$		
7587.04	$(3v_1+3v_2+v_3)^0$		
7609.57	$(4v_2+3v_3)^0$		
7627.14	$(3v_1+v_2+2v_3)^0$		
7681.49	$(2v_2+4v_3)^0$		
7730.08	$6v_1^0$		
7757.29	$(2v_1+7v_2)^0$		
7766.28	$5v_3^0$		
7791.18	$(2v_1+5v_2+v_3)^0$		
7834.97	$(2v_1+3v_2+2v_3)^0$		
7888.16	$(2v_1+v_2+3v_3)^0$		
7909.46	$(5v_1+2v_2)^0$		
7903.54	$(5v_1+v_3)^0$		
7962.27	$(v_1+9v_2)^0$		
8000.93	$(v_1+7v_2+v_3)^0$		
8046.44	$(v_1+5v_2+2v_3)^0$		
8093.61	$(4v_1+4v_2)^0$		
8093.10	$(4v_1+2v_2+v_3)^0$		
8110.13	$(v_1+3v_2+3v_3)^0$		
8120.70	$(4v_1+2v_3)^0$		
8174.27	$(v_1+v_2+4v_3)^0$		

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
8178.27	$11\nu_2^0$	24(LIF,G)	e
8218.84	$(9\nu_2+\nu_3)^0$		
8264.28	$(7\nu_2+2\nu_3)^0$		
8284.17	$(3\nu_1+6\nu_2)^0$		
8299.45	$(3\nu_1+4\nu_2+\nu_3)^0$		
8320.00	$(5\nu_2+3\nu_3)^0$		
8330.35	$(3\nu_1+2\nu_2+2\nu_3)^0$		
8374.58	$(3\nu_1+3\nu_3)^0$		
8382.64	$(3\nu_2+4\nu_3)^0$		
8441.44	$(6\nu_1+\nu_2)^0$		
8457.15	$(\nu_2+5\nu_3)^0$		
8482.12	$(2\nu_1+8\nu_2)^0$		
8507.33	$(2\nu_1+6\nu_2+\nu_3)^0$		
8542.25	$(2\nu_2+4\nu_2+2\nu_3)^0$		
8585.54	$(2\nu_1+2\nu_2+3\nu_3)^0$		
8608.92	$(5\nu_1+\nu_2+\nu_3)^0$		
8623.34	$(5\nu_1+3\nu_2)^0$		
8652.27	$(2\nu_1+4\nu_3)^0$		
8690.72	$(\nu_1+10\nu_2)^0$		
8721.11	$(\nu_1+8\nu_2+\nu_3)^0$		
8758.28	$(\nu_1+6\nu_2+2\nu_3)^0$	24(LIF,G)	e,f
8797.95	$(4\nu_1+3\nu_2+\nu_3)^0$		
8809.81	$(4\nu_1+5\nu_2)^0$		
8817.61	$(4\nu_1+\nu_2+2\nu_3)^0$		
8816.65	$(\nu_1+4\nu_2+3\nu_3)^0$		
8868.35	$(\nu_1+2\nu_2+4\nu_3)^0$		
8911.29	$12\nu_2^0$		
8941.28	$(\nu_1+5\nu_3)^0$		
8944.50	$(10\nu_2+\nu_3)^0$		
8968.55	$7\nu_1^0$		
8982.08	$(8\nu_2+2\nu_3)^0$		
9003.53	$(3\nu_1+7\nu_2)^0$		
9008.77	$(3\nu_1+5\nu_2+\nu_3)^0$		
9029.44	$(6\nu_2+3\nu_3)^0$		
9031.81	$(3\nu_1+3\nu_2+2\nu_3)^0$		
9065.47	$(3\nu_1+\nu_2+3\nu_3)^0$		
9082.71	$(4\nu_2+4\nu_3)^0$		
9101.27	$(6\nu_1+\nu_3)^0$		
9151.35	$(6\nu_1+2\nu_2)^0$		
9148.84	$(2\nu_2+5\nu_3)^0$		
9203.99	$(2\nu_1+9\nu_2)^0$		
9220.73	$(2\nu_1+7\nu_2+\nu_3)^0$		
9226.23	$6\nu_3^0$		
9247.78	$(2\nu_1+5\nu_2+2\nu_3)^0$		
9295.48	$(5\nu_1+2\nu_3)^0$		
9281.74	$(2\nu_1+3\nu_2+3\nu_3)^0$		
9310.32	$(5\nu_1+2\nu_2+\nu_3)^0$		
9334.06	$(5\nu_1+4\nu_2)^0$		
9341.17	$(2\nu_1+\nu_2+4\nu_3)^0$		
9416.05	$(\nu_1+11\nu_2)^0$		
9436.85	$(\nu_1+9\nu_2+\nu_3)^0$		
9468.38	$(\nu_1+7\nu_2+2\nu_3)^0$		
9500.17	$(\nu_1+5\nu_2+3\nu_3)^0$		
9511.96	$(4\nu_1+2\nu_2+2\nu_3)^0$		
9524.14	$(4\nu_1+6\nu_2)^0$		
9518.26	$(4\nu_1+4\nu_2+\nu_3)^0$		
9531.08	$(4\nu_1+3\nu_3)^0$		
9561.06	$(\nu_1+3\nu_2+4\nu_3)^0$		
9623.58	$(\nu_1+\nu_2+5\nu_3)^0$		
9640.29	$13\nu_2^0$		
9672.18	$(7\nu_1+\nu_2)^0$		
9654.17	$(11\nu_2+\nu_3)^0$		
9696.16	$(9\nu_2+2\nu_3)^0$		
9716.70	$(3\nu_1+8\nu_2)^0$		

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
9713.52	$(3\upsilon_1+6\upsilon_2+\upsilon_3)^0$	24(LIF,G)	e,f
9731.72	$(3\upsilon_1+4\upsilon_2+2\upsilon_3)^0$		
9736.30	$(7\upsilon_2+3\upsilon_3)^0$		
9753.30	$(3\upsilon_1+2\upsilon_2+3\upsilon_3)^0$		
9780.98	$(5\upsilon_2+4\upsilon_3)^0$		
9796.80	$(3\upsilon_1+4\upsilon_3)^0$		
9797.03	$(6\upsilon_1+\upsilon_2+\upsilon_3)^0$		
9836.38	$(3\upsilon_2+5\upsilon_3)^0$		
9855.68	$(6\upsilon_1+3\upsilon_2)^0$		
9904.99	$(\upsilon_2+6\upsilon_3)^0$		
9920.43	$(2\upsilon_1+10\upsilon_2)^0$		
9928.47	$(2\upsilon_1+8\upsilon_2+\upsilon_3)^0$		
9950.41	$(2\upsilon_1+6\upsilon_2+2\upsilon_3)^0$		
9984.14	$(5\upsilon_1+\upsilon_2+2\upsilon_3)^0$		
9976.50	$(2\upsilon_1+4\upsilon_2+3\upsilon_3)^0$		
10007.48	$(5\upsilon_1+3\upsilon_2+\upsilon_3)^0$		
10025.10	$(2\upsilon_1+2\upsilon_2+4\upsilon_3)^0$		
10043.14	$(5\upsilon_1+5\upsilon_2)^0$		
10081.20	$(2\upsilon_1+5\upsilon_3)^0$		
10132.49	$(\upsilon_1+12\upsilon_2)^0$		
10161.31	$(\upsilon_1+10\upsilon_2+\upsilon_3)^0$		
10184.66	$8\upsilon_1^0$		
10203.86	$(4\upsilon_1+3\upsilon_2+2\upsilon_3)^0$		
10200.29	$(\upsilon_1+6\upsilon_2+3\upsilon_3)^0$		
10214.37	$(4\upsilon_1+\upsilon_2+3\upsilon_3)^0$		
10231.98	$(4\upsilon_1+7\upsilon_2)^0$		
10251.59	$(\upsilon_1+4\upsilon_2+4\upsilon_3)^0$		
10270.88	$(7\upsilon_1+\upsilon_3)^0$		
10304.69	$(\upsilon_1+2\upsilon_2+5\upsilon_3)^0$		
10352.09	$14\upsilon_2^0$		
10375.23	$(7\upsilon_1+2\upsilon_2)^0$		
10363.42	$(12\upsilon_2+\upsilon_3)^0$		
10399.71	$(\upsilon_1+6\upsilon_3)^0$		
10415.48	$(10\upsilon_2+2\upsilon_3)^0$		
10425.39	$(3\upsilon_1+5\upsilon_2+2\upsilon_3)^0$		
10435.41	$(3\upsilon_1+9\upsilon_2)^0$		
10445.42	$(6\upsilon_1+2\upsilon_3)^0$		
10436.26	$(8\upsilon_2+3\upsilon_3)^0$		
10478.49	$(3\upsilon_1+\upsilon_2+4\upsilon_3)^0$		
10486.21	$(6\upsilon_2+4\upsilon_3)^0$		
10488.24	$(6\upsilon_1+2\upsilon_2+\upsilon_3)^0$		
10522.92	$(4\upsilon_2+5\upsilon_3)^0$		
10557.69	$(6\upsilon_1+4\upsilon_2)^0$		
10582.51	$(2\upsilon_2+6\upsilon_3)^0$		
10632.76	$(2\upsilon_1+11\upsilon_2)^0$		
10630.89	$(2\upsilon_1+9\upsilon_2+\upsilon_3)^0$		
10649.59	$(5\upsilon_1+3\upsilon_3)^0$		
10659.32	$7\upsilon_3^0$		
10663.33	$(2\upsilon_1+5\upsilon_2+3\upsilon_3)^0$		
10697.01	$(5\upsilon_1+4\upsilon_2+\upsilon_3)^0$		
10746.29	$(5\upsilon_1+6\upsilon_2)^0$		
10763.15	$(2\upsilon_1+\upsilon_2+5\upsilon_3)^0$		
10850.34	$(\upsilon_1+13\upsilon_2)^0$		
10876.58	$(\upsilon_1+9\upsilon_2+2\upsilon_3)^0$		
10864.15	$(\upsilon_1+11\upsilon_2+\upsilon_3)^0$		
10900.00	$(4\upsilon_1+4\upsilon_2+2\upsilon_3)^0$		
10916.81	$(4\upsilon_1+6\upsilon_2+\upsilon_3)^0$		
10963.15	$(\upsilon_1+5\upsilon_2+4\upsilon_3)^0$		
11041.86	$(\upsilon_1+\upsilon_2+6\upsilon_3)^0$		
11063.22	$(7\upsilon_1+3\upsilon_2)^0$		
11071.05	$15\upsilon_2^0$		
11096.84	$(6\upsilon_1+\upsilon_2+2\upsilon_3)^0$		
11126.61	$(3\upsilon_1+6\upsilon_2+2\upsilon_3)^0$		
11170.56	$(3\upsilon_1+2\upsilon_2+4\upsilon_3)^0$		
11218.66	$(7\upsilon_2+4\upsilon_3)^0$		

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
11200.80	$(5\upsilon_2+5\upsilon_3)^0$	24(LIF,G)	[e,f]
11259.79	$(6\upsilon_1+5\upsilon_2)^0$		
11251.48	$(3\upsilon_2+6\upsilon_3)^0$		
11290.61	$(5\upsilon_1+3\upsilon_2+2\upsilon_3)^0$		
11347.04	$(2\upsilon_1+8\upsilon_2+2\upsilon_3)^0$		
11364.34	$(2\upsilon_1+12\upsilon_2)^0$		
11376.13	$9\upsilon_1^0$		
11370.18	$(5\upsilon_1+5\upsilon_2+\upsilon_3)^0$		
11401.71	$(8\upsilon_1+\upsilon_3)^0$		
11423.13	$(2\upsilon_1+2\upsilon_2+5\upsilon_3)^0$		
11440.88	$(5\upsilon_1+7\upsilon_2)^0$		
11477.98	$(2\upsilon_1+6\upsilon_3)^0$		
11575.98	$(4\upsilon_1+\upsilon_2+4\upsilon_3)^0$		
11557.26	$(4\upsilon_1+5\upsilon_2+2\upsilon_3)^0$		
11571.20	$(8\upsilon_1+2\upsilon_2)^0$		
11602.15	$(\upsilon_1+6\upsilon_2+4\upsilon_3)^0$		
11804.93	$(3\upsilon_1+7\upsilon_2+2\upsilon_3)^0$		
11933.35	$(4\upsilon_2+6\upsilon_3)^0$		
12101.1	$2\upsilon_1+11\upsilon_2+\upsilon_3$ A-type band	8(IR,G)	Interaction with the $3\nu_2$ level of the low lying $\tilde{A}^2B_2$ electronic state
~12440	$\upsilon_1+14\upsilon_2+\upsilon_3-\upsilon_2$ or $16\upsilon_2+\upsilon_3-\upsilon_2$	11(IR,G)	
13179.45(71)	$(\upsilon_1+14\upsilon_2+\upsilon_3)^0$ or $(16\upsilon_2+\upsilon_3)^0$	11(IR,G)	[a]
13511.057	$(2\upsilon_1+13\upsilon_2+\upsilon_3)^0$ A-type band	10(IR,G)	[a] Interaction with a vibrational level of the low lying $\tilde{A}^2B_2$ electronic state See also 7(IR,G)

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[a] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents one standard deviation.

[b] $(x,y,...)$: band origin and other molecular parameters are obtained from a global fit with other vibration-rotation data, in order to take into account a Coriolis interaction between $x, y, ...$ levels.

[c] Rotational line list available in HITRAN database (21).

[d] Rotational line list available in ATMOS database (22).

[e] Supersonic molecular beam experiment; vibrational level energies calculated from the average of all the values obtained through the different transitions recorded as LIF features (band origins of these transitions measured to within 0.3 cm^{-1}).

[f] Above 9000 cm^{-1}, presence of various resonances between vibrational levels of the ground state. Numerous anomalies in the band positions (shifted by up to 30cm^{-1}) are also observed in this region; they are due to increasingly strong vibronic interaction with levels of the $\tilde{A}^2B_2$ electronic state.

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[23] A. Perrin, C. Camy-Peyret, J.-M. Flaud, and J. Kauppinen, J. Mol. Spectrosc. **130**, 168 (1988).

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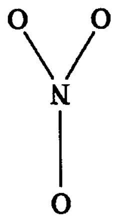
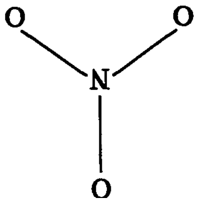
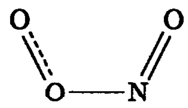
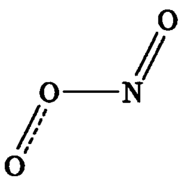
4.3. NO_3

Species	Molecular point group	Normal modes		Activity	
		Symmetry	Vibrations	Raman	Infrared
symmetric 	D_{3h}	A_1' A_2'' E'	ν_1 ν_2 ν_3, ν_4	A I A	I A A
	C_{2v}	A_1 B_1 B_2	$\nu_1 \rightarrow \nu_3$ ν_4 ν_5, ν_6	A A A	A A A
asymmetric (OONO)					
cis 	C_s	A' A''	$\nu_1 \rightarrow \nu_5$ ν_6	A A	A A
trans 	C_s	A' A''	$\nu_1 \rightarrow \nu_5$ ν_6	A A	A A

4.3.a. *sym*-NO_3

It is not yet absolutely clear whether the sym-NO_3 molecule belongs to D_{3h} or C_{2v} symmetry. Both experimental and theoretical works are divided about this point, even if several frequencies are commonly observed. The following table presents the correlation between the normal modes (and their symmetries) when one shifts from the D_{3h} to the C_{2v} symmetry.

D_{3h}			C_{2v}		
A_1'	υ_1	N–O s-stretch	A_1	υ_1	N–O s-stretch
A_2''	υ_2	out of plane bend	B_1	υ_4	out of plane bend
E'	υ_3	N–O a-stretch	A_1	υ_2	N–O s-stretch
			B_2	υ_5	N–O a-stretch
E'	υ_4	a-bend (in plane)	A_1	υ_3	s-bend (in plane)
			B_2	υ_6	a-bend (in plane)

The very latest results published in the literature seem to assess a D_{3h} structure to NO_3. Many anomalies have been observed in the NO_3 spectrum. They mainly find an explanation in perturbations due to the two lowest excited electronic states $\tilde{A}^2E''$ and $\tilde{B}^2E'$. For more details, see Ref. 7 (study of the photoelectron spectrum of NO_3^-), and Refs. 8 and 9(DL,G).

Observed Fundamental Vibrational Frequencies

D_{3h}

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1'	υ_1	N–O s-stretch	1050	1,6(LIF,G); attributed to υ_1 (C_{2v})
			1060	2(LIF,G)
			1080	7 (result obtained from photoelectron spectrum of NO_3^-)
A_2''	υ_2	out of plane bend	749 (or 775)	6(LIF,G); attributed to υ_3 and υ_4 (C_{2v})
			754	1(LIF,G); attributed to υ_3 (C_{2v})
			760	2(LIF,G)
			762.33	4(IR,G)
E'	υ_3	N–O a-stretch (degenerated)	1480	2(LIF,G)
			1489	1(LIF,G); attributed to υ_2 (C_{2v})
			1492.393	3,5(DL,G); 4(IR,G) Could be a vibronic transition (5(DL,G))
			1498	6(LIF,G); attributed to υ_2 (C_{2v})
	υ_4	O–N–O a-bend (in plane - degenerated)	360	1(LIF,G); attributed to υ_6 (C_{2v}) 7 (result obtained from photoelectron spectrum of NO_3^-)
			366	6(LIF,G); attributed to υ_6 (C_{2v})
			380	2(LIF,G)

Observed Fundamental Vibrational Frequencies — Continued

C_{2v}

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1	ν_1	N–O s-stretch	1050	1,6(LIF,G)
			1060	2(LIF,G); attributed to ν_1 (D_{3h})
			1080	7 (result obtained from photoelectron spectrum of NO_3^-); attributed to ν_1 (D_{3h})
	ν_2	N–O s-stretch	1480	2(LIF,G); attributed to ν_3 (D_{3h})
			1489	1(LIF,G)
			1492.393	3,5(DL,G); 4(IR,G); attributed to ν_3 (D_{3h}) Could be a vibronic transition (5(DL,G))
			1498	6(LIF,G)
	ν_3	s-bend (in plane)	749	6(LIF,G)
			754	1(LIF,G)
			760	2(LIF,G); attributed to ν_2 (D_{3h})
			762.33	4(IR,G); attributed to ν_2 (D_{3h})
B_1	ν_4	out of plane bend	775	6(LIF,G)
B_2	ν_5	N–O a-stretch	2000	1(LIF,G)
			2008	6(LIF,G)
	ν_6	a-bend (in plane)	360	1(LIF,G) 7 (result obtained from photoelectron spectrum of NO_3^-); attributed to ν_4 (D_{3h})
			366	6(LIF,G)
			380	2(LIF,G); attributed to ν_4 (D_{3h})

Observed Infrared Bands

Refs. 3,5(DL,G) analysed the ν_3 band (D_{3h} symmetry) and calculated the band origin: $\nu_3^0 = 1492.3929\ (9)^a\ cm^{-1}$. Ref. 4(IR,G) calculated $\nu_2^0 = 762.327\ cm^{-1}$ (D_{3h} symmetry). The other frequencies are presented below. The numbering of the fundamental frequencies refers to D_{3h} or C_{2v} assignments made in the previous tables.

Frequency (cm^{-1})	Assignment	References	Remarks
679	$2\nu_6$ (?)	1(LIF,G)	C_{2v} symmetry
759	$\nu_2+\nu_4-\nu_4$ (?)	4(IR,G)	D_{3h} symmetry
1796	$\nu_1+\nu_3$	1(LIF,G)	C_{2v} symmetry
1910	$2\nu_4+\nu_6$ (?)	1(LIF,G)	C_{2v} symmetry
2024	$5\nu_4$	8(DL,G)	D_{3h} symmetry
2126	$2\nu_1$	1(LIF,G)	C_{2v} symmetry
2155	$\nu_1+3\nu_4$	8(DL,G)	D_{3h} symmetry
2336	$\nu_5+\nu_6$	1(LIF,G)	C_{2v} symmetry
2486	$2\nu_1+\nu_6$	1(LIF,G)	C_{2v} symmetry
2523	$\nu_1+\nu_3$	2(LIF,G)	D_{3h} symmetry See also 5,8,9(DL,G)
2585	$3\nu_2+\nu_4$ or $2\nu_1+\nu_4$	8(DL,G)	D_{3h} symmetry See also 5,9(DL,G)

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[a] Number in parentheses refers to the last quoted digits and represents one standard deviation.

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[3] T. Ishiwata, I. Tanaka, K. Kawaguchi, and E. Hirota, J. Chem. Phys. **82**, 2196 (1985).

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4.3.b. asym-NO$_3$ (OONO)

Theoretical calculations of the six fundamental frequencies were made in Refs. 1 and 5. Only one band was observed and assigned to the N = O stretching motion by several authors:

Frequency (cm^{-1})	References
1830	3(IR,M:O$_2$ + N$_2$)
1834.4 1837.5	4(IR,M:Ar)
1840[a]	1(IR,G)

[a] This band was later reassigned by one of the authors to N$_2$O$_3$ [2(IR,G), erratum on 1(IR,G)].

References

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[2] E. D. Morris, Jr., and H. S. Johnston, J. Chem. Phys. **47**, 4282 (1967).
[3] G. R. Smith, and W. A. Guillory, J. Mol. Spectrosc. **68**, 223 (1977).
[4] S. C. Bhatia, and J. H. Hall, Jr., J. Phys. Chem. **84**, 3255 (1980).
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4.4. N$_2$O

Species	Molecular point group	Normal modes		Activity	
		Symmetry	Vibrations	Raman	Infrared
N—N—O	C$_{\infty v}$	Σ^+ Π	ν_1, ν_3 ν_2	A A	A A

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
Σ^+	ν_1	N–O stretch	1284.9033	1,2 and references therein
Π	ν_2	bend	588.7678	1,2 and references therein
Σ^+	ν_3	N–N stretch	2223.7567	1,2 and references therein

Observed Infrared Bands

About seventy bands including fundamental, overtone and combination bands have been observed for $^{14}N_2{}^{16}O$ between 525 and 5130 cm^{-1}. The band origins and a list of rotational line positions are available in HITRAN[1] and ATMOS[2] databases. Since, to our knowledge, no major new contribution to these data exists, we only reproduce HITRAN[1] here the list ATMOS[2] of the observed infrared bands published by Ref. 1 and/or Ref. 2 without further references, in order to make these tables complete for the user. For more details, we refer the reader to the works mentioned in Ref. 1 and Ref. 2.

Observed Infrared Bands

Frequency (cm^{-1})	Assignment							
	Upper state				Lower state			
	ν_1	ν_2	l_2	ν_3	ν_1	ν_2	l_2	ν_3
571.320	0	3	1	0	0	2	2	0
579.364	0	2	0	0	0	1	1	0
580.934	0	3	1	0	0	2	0	0
588.768	0	1	1	0	0	0	0	0
588.978	0	2	2	0	0	1	1	0
589.168	0	3	3	0	0	2	2	0
595.361	1	1	1	0	1	0	0	0
696.140	1	0	0	0	0	1	1	0
938.8534	0	0	0	1	1	0	0	0
1055.6245	0	0	0	1	0	2	0	0
1153.3768	0	4	2	0	0	2	2	0
1154.4408	0	4	0	0	0	2	0	0
1160.2973	0	3	1	0	0	1	1	0
1168.1323	0	2	0	0	0	0	0	0
1177.0931	1	2	0	0	1	0	0	0

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment							
	Upper state				Lower state			
	ν_1	ν_2	l_2	ν_3	ν_1	ν_2	l_2	ν_3
1177.7446	0	2	2	0	0	0	0	0
1278.4361	2	0	0	0	1	0	0	0
1284.9033	1	0	0	0	0	0	0	0
1285.5879	2	1	1	0	1	1	1	0
1291.4979	1	1	1	0	0	1	1	0
1293.8642	1	2	0	0	0	2	0	0
1297.0540	1	2	2	0	0	2	2	0
1297.1477	1	3	1	0	0	3	1	0
1301.8084	1	3	3	0	0	3	3	0
1395.2071	2	0	0	0	0	2	0	0
1620.5479	0	1	1	1	0	2	2	0
1630.1603	0	1	1	1	0	2	0	0
1634.9889	0	0	0	1	0	1	1	0
1733.8051	0	4	0	0	0	1	1	0
1742.3536	0	4	2	0	0	1	1	0
1749.0651	0	3	1	0	0	0	0	0
1868.4682	1	3	1	0	0	2	2	0
1873.2286	1	2	0	0	0	1	1	0
1878.0806	1	3	1	0	0	2	0	0
1880.2657	1	1	1	0	0	0	0	0
1880.9503 [a]	2	1	1	0	1	0	0	0
1886.0307	1	2	2	0	0	1	1	0
1890.9760	1	3	3	0	0	2	2	0
1974.5715	2	0	0	0	0	1	1	0
2079.0746 [a]	0	2	0	1	1	0	0	0
2181.3724	0	3	3	1	0	3	3	0
2181.6967	0	6	0	0	1	0	0	0
2181.7137	1	1	1	1	1	1	1	0
2182.1823	0	3	1	1	0	3	1	0
2189.5466	0	6	2	0	1	0	0	0
2193.6210	0	0	0	2	0	0	0	1
2195.3966	0	2	2	1	0	2	2	0
2195.8457	0	2	0	1	0	2	0	0
2195.9158	1	0	0	1	1	0	0	0
2209.5247	0	1	1	1	0	1	1	0
2223.7568	0	0	0	1	0	0	0	0
2309.0455	0	5	1	0	0	1	1	0
2322.5731	0	4	0	0	0	0	0	0
2331.1215	0	4	2	0	0	0	0	0
2452.8106	1	4	0	0	0	2	0	0
2453.8452	1	4	2	0	0	2	2	0
2457.4449	1	3	1	0	0	1	1	0
2461.9965	1	2	0	0	0	0	0	0
2463.3484	2	2	0	0	1	0	0	0
2474.7987	1	2	2	0	0	0	0	0
2551.4678	3	0	0	0	1	0	0	0
2563.3394	2	0	0	0	0	0	0	0
2566.1169 [b]	3	1	1	0	1	1	1	0
2577.0857	2	1	1	0	0	1	1	0
2580.1195	2	2	0	0	0	2	0	0

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment							
	Upper state				Lower state			
	ν_1	ν_2	l_2	ν_3	ν_1	ν_2	l_2	ν_3
2586.7349	2	3	1	0	0	3	1	0
2588.3078	2	2	2	0	0	2	2	0
2668.2388 [b]	3	0	0	0	0	2	0	0
2753.5028 [b]	0	3	1	1	0	2	2	0
2763.1240 [c]	0	3	1	1	0	2	0	0
2770.5940 [c]	0	3	3	1	0	2	2	0
2775.2070 [c]	0	2	0	1	0	1	1	0
2777.0758 [b]	1	1	1	1	1	0	0	0
2784.3700 [c]	0	2	2	1	0	1	1	0
2798.2900 [c]	0	1	1	1	0	0	0	0
3342.491	0	3	1	1	0	1	1	0
3363.974	0	2	0	1	0	0	0	0
3445.921	2	0	0	1	1	0	0	0
3462.030	1	2	0	1	0	2	0	0
3464.713	1	2	2	1	0	2	2	0
3473.212	1	1	1	1	0	1	1	0
3480.821	1	0	0	1	0	0	0	0
3620.941	1	4	0	0	0	0	0	0
3747.031	2	3	1	0	0	1	1	0
3748.252	2	2	0	0	0	0	0	0
3836.373	3	0	0	0	0	0	0	0
3857.612	3	1	1	0	0	1	1	0
4061.979	1	1	1	1	0	0	0	0
4335.798	2	3	1	0	0	0	0	0
4388.928	0	1	1	2	0	1	1	0
4417.379	0	0	0	2	0	0	0	0
4630.164	1	2	0	1	0	0	0	0
4730.408	2	1	1	1	0	1	1	0
4730.828	2	0	0	1	0	0	0	0
4977.695	0	1	1	2	0	0	0	0
5026.34	3	2	0	0	0	0	0	0
5105.65	4	0	0	0	0	0	0	0

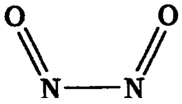
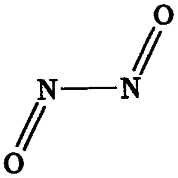
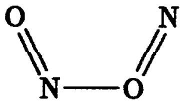
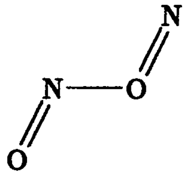
[a] Rotational line list available in HITRAN database[1] only.
[b] Rotational line list available in ATMOS database[2] only.
[c] Band origin measurements from ATMOS database[2]; other results are presented in HITRAN database[1].

References

[1] The HITRAN database: 1986 edition, L. S. Rothman, R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C. P. Rinsland, and M. A. H. Smith, Appl. Opt. **26**, 4058 (1987).

[2] Molecular line parameters for the Atmospheric Trace MOlecule Spectroscopy experiment, L. R. Brown, C. B. Farmer, C. P. Rinsland, and R. A. Toth, Appl. Opt. **26**, 5154 (1987).

4.5. $(NO)_2$

Species	Molecular point group	Normal modes		Activity	
		Symmetry	Vibrations	Raman	Infrared
cis-O=N–N=O 	C_{2v}	A_1	$\nu_1 \rightarrow \nu_3$	A	A
		A_2	ν_4	A	I
		B_2	ν_5, ν_6	A	A
trans-O=N–N=O 	C_{2h}	A_g	$\nu_1 \rightarrow \nu_3$	A	I
		A_u	ν_4	I	A
		B_u	ν_5, ν_6	I	A
cis-O=N–O=N 	C_s	A'	$\nu_1 \rightarrow \nu_5$	A	A
		A''	ν_6	A	A
trans-O=N–O=N[a] 	C_s	A'	$\nu_1 \rightarrow \nu_5$	A	A
		A''	ν_6	A	A

[a] Not observed.

4.5.a. *cis*-O=N–N=O

This species is reported as the most stable one. Useful information on the molecular structure of this isomer is presented in Ref. 8.

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1	ν_1	N=O s-stretch	1861	IR : 1(L); 2(M:CO_2); 4(G); 6(S); 11(G) Ra : 1(L); 7(M:CO_2)
			1868.252	IR : 1(S); 2(M:Ar); 3(M:N_2); 9(LXe); 13(G); 14(M:Ne) Ra : 5,6,10(S)
	ν_2	N–N stretch	264	IR : 11(G) Ra : 1(L); 5,6,10(S); 7(M:CO_2)
			273	IR : 5(S)
	ν_3	N–N=O s-bend	161	Ra : 7(M:CO_2)
			169	IR : 11(G) Ra : 1(L)
			176	Ra : 5(S)
			187	IR : 5(S) Ra : 6,10(S)
A_2	ν_4	torsion	88.2	IR: 11(G); from $\nu_5-\nu_4=1700.8$ cm^{-1}
			97	Ra : 5,6(S); 10(S)
B_2	ν_5	N=O a-stretch	1760	IR : 1,5,6(S); 9(LXe) Ra : 1(L); 10(S)
			1769	IR : 1(L); 2(M:CO_2)
			1776	IR : 2(M:Ar); 3(M:N_2)
			1778.7 1780.6	IR : 14(M:Ne)
			1789	IR : 4,11,12,13(G)
	ν_6	N–N=O a-bend	199	IR : 11(G) Ra : 1(L); 6(S); 7(M:CO_2)
			214	Ra : 10(S)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
97	v_4	10(Ra,S)	$T=12$ K See also 5,6(Ra,S); 6(IR,S); 11(IR,G)
170	v_3	11(IR,G)	$T=118\rightarrow138$ K See also 1(Ra,L); 5,6,10(Ra,S); 5(IR,S); 7(Ra,M)
198	v_6	11(IR,G)	$T=118\rightarrow138$ K See also 1(Ra,L); 6,10(Ra,S); 7(Ra,M)
199	$2v_4$	10(Ra,S)	$T=12$ K See also 6(Ra,S)
263	v_2	11(IR,G)	$T=118\rightarrow138$ K See also 1(Ra,L); 5,6(IR,S); 6,10(Ra,S); 7(Ra,M)
347	v_2+v_4	10(Ra,S)	$T=12$ K
401	$2v_4+v_6$ or $2v_6$	10(Ra,S)	$T=12$ K; if $v_6=199$ cm^{-1}
491	v_2+v_6 or $2v_6$	10(Ra,S)	$T=12$ K; if $v_6=214$ cm^{-1} See also 1(Ra,L); 1(IR,S); 6(Ra+IR,S)
519	$2v_2$	1(IR,S)	
1506	v_5-v_2	1(IR,L)	
1545	v_5-v_6 (?)	1(IR,L)	
1600	v_1-v_2	1(IR,L)	See also 1(IR,S)
1653	v_1-v_6 (?)	4(IR,G)	
1700.8	v_5-v_4 or v_1-v_3 (?)	11(IR,G)	$T=118\rightarrow138$ K See also 4(IR,G)
1732 1759 1770 1774.6	$v_i+v_5-v_i$ (?) $i=3,4$ or 6	11(IR,G)	$T=118\rightarrow138$ K
1789.15	v_5 A-type band	13(IR,G)	Q head See also 1(Ra+IR,L); 1,5,6(IR,S); 2,3,14(IR,M); 4,11,12(IR,G); 9(IR,LXe); 10(Ra,S)
1860	v_1	11(IR,G)	$T=118\rightarrow138$ K See also 1(Ra+IR,L); 1,6(IR,S); 2,3,14(IR,M); 4(IR,G); 5,6,10(Ra,S); 7(Ra,M); 9(IR,LXe)
1868.2515(3)	v_1^0	13(IR,G)	[a]
1918	v_3+v_5	1(IR,S)	
1965	v_5+v_6	4(IR,G)	See also 1(IR,L+S)
2030 2042	v_2+v_5	4(IR,G)	See also 1(IR,L+S)
2124–2130	v_1+v_2	1(IR,L+S)	
3551	$2v_5$	11(IR,G)	$T=118\rightarrow138$ K; Q head See also 1(IR,L+S); 4(IR,G)
3559.32(10)	$2v_5^0$	15(IR,G)	[a]
3626	v_1+v_5	11(IR,G)	$T=118\rightarrow138$ K; Q head See also 1(IR,L+S); 4(IR,G); 9(IR,LXe)
3626.45(10)	$(v_1+v_5)^0$	15(IR,G)	[a]
3708	$2v_1$	1(IR,L)	See also 1(IR,S); 9(IR,LXe)
5200±30	$3v_5$ (?)	1(IR,L)	See also 1(IR,S)
5390±30	$2v_1+v_5$	1(IR,L)	See also 1(IR,S)

[a] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents one standard deviation.

References

[1] A. L. Smith, W. E. Keller, and H. L. Johnston, J. Chem. Phys. 19, 189 (1951).
[2] W. G. Fateley, H. A. Bent, and B. Crawford, Jr., J. Chem. Phys. 31, 204 (1959).
[3] W. A. Guillory and C. E. Hunter, J. Chem. Phys. 50, 3516 (1969).
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[6] A. Anderson and B. Lassier-Govers, Chem. Phys. Lett. 50, 124 (1977).
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[11] V. Menoux, R. Le Doucen, C. Haeusler, and J. C. Deroche, Can. J. Phys. 62, 322 (1984).
[12] Ph. Brechignac, S. De Benedictis, N. Halberstadt, B. J. Whitaker, and S., Avrillier, J. Chem. Phys. 83, 2064 (1985).
[13] Y. Matsumoto, Y. Ohshima, and M. Takami, J. Chem. Phys. 92, 937 (1990).
[14] M. E. Jacox and W. E. Thompson, J. Chem. Phys. 93, 7609 (1990).
[15] J. R. Hetzler, M. P. Casassa, and D. S. King, J. Phys. Chem. 95, 8086 (1991).

4.5.b. *trans*-O=N–N=O

The only mode attributed to this species is the N=O a-stretch ν_5. It has been observed through matrix experiments, in infrared spectra. Nevertheless, these assignments have to be considered rather cautiously :

Frequency (cm^{-1})	References
1740	1(IR, M:CO$_2$)
1760.6 1762.5	3(IR, M:Ne)
1764	2(IR, M:N$_2$)

References

[1] W. G. Fateley, H. A. Bent, and B. Crawford, Jr., J. Chem. Phys. 31, 20 (1959).
[2] W. A. Guillory and C. E. Hunter, J. Chem. Phys. 50, 3516 (1969).
[3] M. E. Jacox and W. E. Thompson, J. Chem. Phys. 93, 7609 (1990).

4.5.c. *cis*-O=N–O=N

A "red species" has been observed, in special conditions, by only one group of workers[1]. It results from the reaction of NO with Lewis acids (BF$_3$, BCl$_3$, BBr$_3$, SnCl$_4$, SiF$_4$, TiCl$_4$), or with HCl, or with SO$_2$, and it has been identified as the asymmetric *cis*-(NO)$_2$ species. Raman and infrared spectra have been recorded at 77 K. We reproduce here the fundamental frequencies obtained from Raman spectra of the products of the NO + BCl$_3$ reaction. Unless specified, the other frequencies (combination or overtone bands) were also obtained from these spectra.

The frequencies resulting from data recorded for different chemical conditions, detailed in Ref. 1, agree within 10 cm^{-1} with those presented here.

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	Remarks
A'	ν_1	–O=N stretch	1778	Could be ν_2
	ν_2	–N=O stretch	1690	Could be ν_1
	ν_3	=N–O= stretch	482	
	ν_4	O=N–O= bend	184	Could be ν_5
	ν_5	N=O–N= bend	116	Could be ν_4
A''	ν_6	torsion	–	

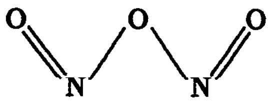
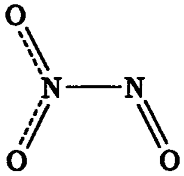
Observed Infrared Bands

Frequency (cm^{-1})	Assignment	Remarks
116	ν_5	
184	ν_4	
296	$\nu_4+\nu_5$ or $\nu_3-\nu_4$	
371	$2\nu_4$	
482	ν_3	
552	$3\nu_4$	
593	$2\nu_3-2\nu_4$	
672	$\nu_3+\nu_4$	
744	$4\nu_4$	
778	$2\nu_3-\nu_4$	
849	$\nu_3+2\nu_4$	
925	$5\nu_4$	
962	$2\nu_3$	
1038	$\nu_3+3\nu_4$	NO+HCl
1151	$2\nu_3+\nu_4$	NO+HCl
1197	$\nu_2-\nu_3$	NO+HCl
1342	$2\nu_3+2\nu_4$	NO+HCl
1690	ν_2	
1778	ν_1	
1873	$\nu_2+\nu_4$	
1957	$\nu_1+\nu_4$	
1994	$\nu_2+(\nu_4+\nu_5)$ or $\nu_2+(\nu_3-\nu_4)$	
2061	$\nu_2+2\nu_4$	
2137	$\nu_1+2\nu_4$	NO+HCl
2176	$\nu_2+\nu_3$	
2237	$\nu_2+3\nu_4$	
2345	$\nu_2+(\nu_3+\nu_4)$	NO+HCl
3363	$2\nu_2$	
3450	$\nu_1+\nu_2$	NO+HCl;IR
3469	$2\nu_2+\nu_5$	
3541	$2\nu_2+\nu_4$	
3738	$2\nu_1+\nu_4$ or $2\nu_2+2\nu_4$	NO+HCl;IR

Reference

[1] J. R. Ohlsen, and J. Laane, J. Am. Chem. Soc. 100, 6948 (1978).

4.6. N_2O_3

Species	Molecular point group	Normal mdes		Activity	
		Symmetry	Vibrations	Raman	Infrared
Symmetric 	C_{2v}	A_1	$\nu_1 \rightarrow \nu_4$	A	A
		A_2	ν_5	A	A
		B_1	ν_6	A	A
		B_2	$\nu_7 \rightarrow \nu_9$	A	A
Asymmetric 	C_s	A'	$\nu_1 \rightarrow \nu_7$	A	A
		A''	ν_8, ν_9	A	A

4.6.a. *sym*-N_2O_3

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1	ν_1	N=O s-stretch	1740	Ra : 2(M:NO)
	ν_2	N–O s-stretch	967	IR : 1(M:N_2); 3(LXe)
			973.6	IR : 2(M:NO); 4(M:Ne) Ra : 2(M:NO)
	ν_3	N–O–N bend	375	IR : 3(LXe); could be ν_4
			388	IR : 1(M:N_2)
			395	Ra : 2(M:NO)
	ν_4	O=N–O s-bend	345	Ra : 2(M:NO)
			366	IR : 1(M:N_2)
			375	IR : 3(LXe); could be ν_3
A_2	ν_5	torsion	140	Ra : 2(M:NO)
B_1	ν_6	torsion	105	Ra : 2(M:NO); calculated from $2\nu_6 = 210\ cm^{-1}$
B_2	ν_7	N=O a-stretch	1661	IR : 1(M:N_2)
			1679	Ra : 2(M:NO)
			1689	IR : 1(M:N_2); 2(M:NO); 3(LXe)
			1697.2	IR : 4(M:Ne)
	ν_8	N–O a-stretch	865	IR : 2(M:NO)
			877	IR : 1(M:N_2)
	ν_9	O=N–O a-bend	705	IR : 1(M:N_2); 2(M:NO)
			710	Ra : 2(M:NO)

Observed Infrared Bands

No other bands were observed, apart the fundamental ones mentioned above.

References

[1] E. L. Varetti and G. C. Pimentel, J. Chem. Phys. 55, 3813 (1971).
[2] E. M. Nour, L.-H. Chen, and J. Laane, J. Phys. Chem. 87, 1113 (1983).
[3] R. F. Holland and W. B. Maier II, J. Chem. Phys. 78, 2928 (1983).
[4] M. E. Jacox and W. E. Thompson, J. Chem. Phys. 93, 7609 (1990).

4.6.b. *asym*-N_2O_3

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	N=O stretch	1829.54	IR : 3,7(G); 6(LXe); 8(M:Ne) Band origin calculated from band shape simulations
			1840	IR : 2(M:N_2)
			1860	IR,Ra : 5(M:NO)
			1867	IR : 1(M:O_2)
	ν_2	NO_2 a-stretch	1594	IR : 1(M:O_2); 5(M:NO) Ra : 5(M:NO)
			1627	IR : 2(M:N_2); 6(LXe)
			1643.3	IR : 8(M:Ne)
			1652	IR : 3(G)
	ν_3	NO_2 s-stretch	1288	Ra : 5(M:NO)
			1296	IR : 5(M:NO); 6(LXe)
			1302.5	IR : 1(M:O_2); 2(M:N_2); 3(G); 8(M:Ne)
	ν_4	NO_2 bend	773.1	IR : 2(M:N_2); 3(G); 6(LXe) 8(M:Ne)
			788	IR : 1(M:O_2); 5(M:NO) Ra : 5(M:NO)
	ν_5	NO_2 rock	395	IR : 5(M:NO)
		out of phase	405	Ra : 5(M:NO)
		(or NO_2 rock)	413	IR : 3(G); 6(LXe)
			420	IR : 2(M:N_2)
	ν_6	N–N stretch	243	IR : 3(G); 6(LXe)
			263	IR : 4(L); 5(M:NO) Ra : 5(M:NO)
	ν_7	NO_2 rock	160	IR : 4(L)
		in phase	203	IR,Ra : 5(M:NO)
		(or wag in plane)		
A''	ν_8	NO_2 wag	615.5	IR : 6(LXe)
		(out of plane)	626	IR,Ra : 5(M:NO)
	ν_9	torsion	63	IR : 3(G)
			70	IR,Ra : 5(M:NO)
			76	IR : 4(L)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
70	ν_9	5(Ra,M:NO)	$T=12$ K See also 3(IR,G); 4(IR,L)
205	ν_7	5(Ra,M:NO)	$T=12$ K See also 4(IR,L)
244(1)	ν_6	6(IR,LXe)	[b] $T=165$ K See also 3(IR,G); 4(IR,L); 5(Ra+IR,M)
330 337 346 355	$\nu_5-\nu_9+n\nu_9-n\nu_9$	3(IR,G)	$T=220$ K; Q heads C-type bands See also 6(IR,LXe)
370	$\nu_8-\nu_6$	5(Ra,M:NO)	$T=12$ K

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
408 P 419 R	υ_5 (a,B)-type band	3(IR,G)	$T=220$ K See also 2,5(IR,M); 5(Ra,M); 6(IR,LXe)
455 462 469 477	$(\upsilon_5+\upsilon_9)+3\upsilon_9-3\upsilon_9$ $(\upsilon_5+\upsilon_9)+2\upsilon_9-2\upsilon_9$ $(\upsilon_5+\upsilon_9)+\upsilon_9-\upsilon_9$ $\upsilon_5+\upsilon_9$	3(IR,G)	$T=220$ K; Q heads C-type bands See also 6(IR,LXe): the authors attributed $2\upsilon_6$ to 477 cm^{-1}
525(1)	$\upsilon_3-\upsilon_4$ (?)	6(IR,LXe)	[b] $T=165$ K; could be $\upsilon_4-\upsilon_6$ (see below)
532 545 557 570	$\upsilon_4-\upsilon_6$ $(\upsilon_4-\upsilon_6)+\upsilon_9-\upsilon_9$ $(\upsilon_4-\upsilon_6)+2\upsilon_9-2\upsilon_9$ $(\upsilon_4-\upsilon_6)+3\upsilon_9-3\upsilon_9$	3(IR,G)	$T=220$ K; Q heads (A,b)- or (A,B)-type bands
565	$\upsilon_8-\upsilon_9$ (?)	5(Ra,M:NO)	$T=12$ K; could belong to the sequence above
615.5(1.0)	υ_8	6(IR,LXe)	[b] $T=165$ K See also 5(Ra+IR,M)
767 P 779 R	υ_4 (a,B)-type band	3(IR,G)	$T=220$ K See also 1,2,5,8(IR,M): 5(Ra,M); 6(IR,LXe)
803(1)	$\upsilon_8+\upsilon_7$	6(IR,LXe)	[b] $T=165$ K
822(1)	$2\upsilon_5$	6(IR,LXe)	[b] $T=165$ K
993 1001 1010	$(\upsilon_4+\upsilon_6)+2\upsilon_9-2\upsilon_9$ $(\upsilon_4+\upsilon_6)+\upsilon_9-\upsilon_9$ $\upsilon_4+\upsilon_6$	3(IR,G)	$T=220$ K See also 6(IR,LXe)
1298 P 1305 Q 1313 R	υ_3 (A,b)-type band	3(IR,G)	$T=220$ K See also 1,2,5,8(IR,M); 5(Ra,M); 6(IR,LXe)
1378(1)	$\upsilon_4+\upsilon_8$	6(IR,LXe)	[b] $T=165$ K
1426(1)	$\upsilon_3+\upsilon_7$ (?)	6(IR,LXe)	[b] If $\upsilon_7=160$ cm^{-1}; $T=165$ K
1485(1)	$\upsilon_3+\upsilon_7$ (?)	6(IR,LXe)	[b] If $\upsilon_7=203$ cm^{-1}; $T=165$ K
1535(1)	$2\upsilon_4$ or $\upsilon_3+\upsilon_6$	6(IR,LXe)	[b] $T=165$ K
1646 P 1658 R	υ_2 (a,B)-type band	3(IR,G)	$T=220$ K See also 1,2,5,8 (IR,M); 5(Ra,M); 6(IR,LXe)
1826.0 1827.5	$(\upsilon_1+2\upsilon_9-2\upsilon_9)^0$ $(\upsilon_1+\upsilon_9-\upsilon_9)^0$	7(IR,G)	$T=232$ K Band origins calculated from the shifts between Q heads in the υ_1 band region
1827.7	$(\upsilon_1+(\upsilon_7+\upsilon_9)-(\upsilon_7+\upsilon_9))^0$	7(IR,G)	Same remarks as for $\upsilon_1+n\upsilon_9-n\upsilon_9$
1828.9	$(\upsilon_1+\upsilon_7-\upsilon_7)^0$	7(IR,G)	Same remarks as for $\upsilon_1+n\upsilon_9-n\upsilon_9$

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
1829.535(2)	ν_1^0	7(IR,G)	^{a,c} $T=232$ K
1821.3 P 1829.5 Q 1838.3 R	ν_1 (A,B)-type band	7(IR,G)	$T=232$ K See also 1,2,5,8(IR,M); 3(IR,G); 5(Ra,M); 6(IR,LXe)
1829.9	$(\nu_1+(\nu_6+\nu_9)-(\nu_6+\nu_9))^0$	7(IR,G)	Same remarks as for $\nu_1+n\nu_9-n\nu_9$
1831.6	$(\nu_1+\nu_6-\nu_6)^0$	7(IR,G)	Same remarks as for $\nu_1+n\nu_9-n\nu_9$
2028(1)	$\nu_2+\nu_5$	6(IR,LXe)	^{b} $T=165$ K
2072(1)	$\nu_1+\nu_6$	6(IR,LXe)	^{b} $T=165$ K
2444(1)	$\nu_1+\nu_8$	6(IR,LXe)	^{b} $T=165$ K
2580(1)	$2\nu_3$	6(IR,LXe)	^{b} $T=165$ K
2598(1)	$\nu_1+\nu_4$	6(IR,LXe)	^{b} $T=165$ K
2900(1)	$\nu_2+\nu_3$	6(IR,LXe)	^{b} $T=165$ K
3123(1)	$\nu_1+\nu_3$	6(IR,LXe)	^{b} $T=165$ K
3227(1)	$2\nu_2$	6(IR,LXe)	^{b} $T=165$ K
3456(1)	$\nu_1+\nu_2$	6(IR,LXe)	^{b} $T=165$ K
3618.7 3621.3 3624.4	$(2\nu_1+3\nu_9-3\nu_9)^0$ $(2\nu_1+2\nu_9-2\nu_9)^0$ $(2\nu_1+\nu_9-\nu_9)^0$	7(IR,G)	$T=232$ K Band origins calculated from the shifts between Q heads in the $2\nu_1$ band region
3625.5(1.0)	$2\nu_1$	6(IR,LXe)	^{b} $T=165$ K
3628.03(5)	$2\nu_1^0$	7(IR,G)	^{a,c} $T=232$ K
3633.3 3639.1	$(2\nu_1+\nu_6-\nu_6)^0$ $(2\nu_1+2\nu_6-2\nu_6)^0$	7(IR,G)	Same remarks as for $2\nu_1+n\nu_9-n\nu_9$
3866(1)	$3\nu_3$	6(IR,LXe)	^{b} $T=165$ K
5386.7	$(3\nu_1+\nu_9-\nu_9)^0$	7(IR,G)	$T=232$ K Band origin calculated from the shifts between Q heads in the $3\nu_1$ band region
5392.6	$(3\nu_1+\nu_7-\nu_7)^0$	7(IR,G)	Same remarks as for $3\nu_1+\nu_9-\nu_9$
5394.124(10)	$3\nu_1^0$	7(IR,G)	^{a,c} $T=232$ K

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
5404.2	$(3\upsilon_1+\upsilon_6-\upsilon_6)^0$	7(IR,G)	Same remarks as for $3\upsilon_1+\upsilon_9-\upsilon_9$
7128.5(1.0)	$4\upsilon_1^0$	7(IR,G)	[b,c] $T=232$ K

[a] Number in parentheses refers to the last quoted digits and represents one standard deviation

[b] Number in parentheses refers to the last quoted digits and represents the absolute accuracy of line position measurements

[c] Band shape simulation

References

[1] W. G. Fateley, H. A. Bent, and B. Crawford, Jr., J. Chem. Phys. 31, 204 (1959).

[2] E. L. Varetti and G. C. Pimentel, J. Chem. Phys. 55, 3813 (1971).

[3] C. H. Bibart and G. E. Ewing, J. Chem. Phys. 61, 1293 (1974).

[4] G. M. Bradley, W. Siddall, H. L. Strauss, and E. L. Varetti, J. Phys. Chem. 79, 1949 (1975).

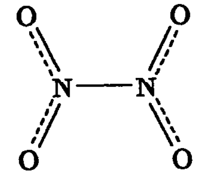
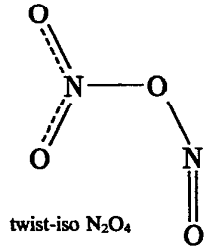
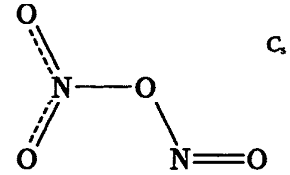
[5] E. M. Nour, L.-H. Chen, and J. Laane, J. Phys. Chem. 87, 1113 (1983).

[6] R. F. Holland and W. B. Maier II, J. Chem. Phys. 78, 2928 (1983).

[7] L. A. Chewter, I. W. M. Smith, and G. Yarwood, Mol. Phys. 63, 843 (1988).

[8] M. E. Jacox and W. E. Thompson, J. Chem. Phys. 93, 7609 (1990).

4.7. N_2O_4

Species	Molecular point group	Normal modes Symmetry	Normal modes Vibrations	Activity Raman	Activity Infrared
symmetric					
	D_{2h}	A_g	$\nu_1 \rightarrow \nu_3$	A	I
		A_u	ν_4	I	I
		B_{1g}	ν_5, ν_6	A	I
		B_{1u}	ν_7	I	A
sym-N_2O_4		B_{2g}	ν_8	A	I
or		B_{2u}	ν_9, ν_{10}	I	A
D_{2h} N_2O_4		B_{3u}	ν_{11}, ν_{12}	I	A
staggered[a]					
cfr. symmetric, but	D_{2d}	A_1	$\nu_1 \rightarrow \nu_3$	A	I
the NO_2 planes		B_1	ν_4	A	I
are perpendicular		B_2	ν_5, ν_6	A	A
to each other		E	$\nu_7 \rightarrow \nu_9$	A	A
D-type[b]					
	C_s	A'	$\nu_1 \rightarrow \nu_9$	A	A
twist-iso N_2O_4		A''	$\nu_{10} \rightarrow \nu_{12}$	A	A
D'-type[b]					
	C_s	A'	$\nu_1 \rightarrow \nu_9$	A	A
		A''	$\nu_{10} \rightarrow \nu_{12}$	A	A

---

[a] Not observed.

[b] *D* and *D'*-types N_2O_4 are often called *asym*- or *iso*-N_2O_4, without distinction. It is not yet obvious which molecular structure belongs to *D* or *D'*-type.

4.7.a. *sym*-N_2O_4

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_g	ν_1	N–O s-stretch	1380	Ra : 1,11(L); 6(S)
		in phase	1383	1,10(S); 4(M:Ar); 7(M:Ne)
			1387	7(M:Xe)
	ν_2	NO_2 bend	807	Ra : 1(L); 6(S); 7(M:Ne)
		in phase	811	1,10(S); 11(L)
			814	4(M:Ar); 7(M:Xe)
	ν_3	N–N stretch	257	Ra : 7(M:Xe)
			262	4(M:Ar)
			267	1,11(L); 7(M:Ne)
			275	1(S)
			282	6,10,13(S)
A_u	ν_4	torsion	79	Deduced from the band sequence around 540 cm^{-1} (5(IR,G))
B_{1g}	ν_5	N–O a-stretch	1712	Ra : 1(L)
		out of phase	1718	7(M:Xe)
			1725	1,6,10(S)
	ν_6	NO_2 rock	484	Ra : 1(L); 7(M:Xe)
		out of phase	491	1(S)
		(or NO_2 rock)	498	6,10,13(S); 7(M:Ne)
B_{1u}	ν_7	NO_2 wag	423	IR : 1(L); 5(G); 8(LXe)
		in phase	429	1(G)
		(out of plane)	436	6,12(S)
B_{2g}	ν_8	NO_2 wag	657	Ra : 7(M:Xe)
		out of phase	672	1(L)
		(out of plane)	677	6,10(S)
B_{2u}	ν_9	N–O a-stretch	1735	IR : 1(L); 2(M:Ar);
		in phase		3(M:N_2); 6(S)
			1742	8(LXe)
			1749.2	1(G); 2(M:O_2); 9(M:Ar); 12(S)
			1756.76	5,14,15(G)
	ν_{10}	NO_2 rock	265	IR : 6(S); in agreement
		in phase		with the predicted
		(or NO_2 wag in plane)		value of 5(G)
			375	8(LXe)
			381	1(G)
			635	12(S)
B_{3u}	ν_{11}	N–O s-stretch	1250	IR : 6,12(S); 8(LXe)
		out of phase	1257	1(L); 2,9(M:Ar);
			1261.1	1,14(G); 2(M:O_2); 3(M:N_2)
			1264	5(G)
	ν_{12}	NO_2 bend	742	IR : 1(L); 6,12(S); 8(LXe)
		out of phase	746	2(M:Ar,O_2); 9(M:Ar)
			751.3	1,5,14(G); 3(M:N_2)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
265(1)	ν_{10} (?)	6(IR,S)	[a] $T = 20$ K See below for other suggestions
281.3	ν_3	10,13(Ra,S)	$T = 80$ and 20 K respectively See also 1,6(Ra,S); 1,11(Ra,L); 4,7(Ra,M)
375	ν_{10} (?)	8(IR,LXe)	$T = 165$ K See also 1(IR,G)
370.3(2) 375.8(2) 380.1(2) 386.0(2)	$(\nu_2 - \nu_7) + n\nu_4 - n\nu_4$	5(IR,G)	[a] $T = 203$ K; Q heads C-type bands
404.7(2) 416.4(2) 420.7(2) 424.9(2) 429.5(2) 435.4(2) 442.2(2) 446.9(2) 451.9(2) 457.8(2)	$\nu_7 + n\nu_4 - n\nu_4$	5(IR,G)	[a] $T = 203$ K
435.8	ν_7	12(IR,S)	$T = 20$ K See also 1(IR,L); 1,5(IR,G); 6(IR,S); 8(IR,LXe)
498.2	ν_6	10(Ra,S)	$T = 80$ K See also 1(Ra,L); 1,6,13(Ra,S); 7(Ra,M)
522.5(2) 526.0(2) 529.0(2) 533.5(2) 538.3(2) 542.8(2) 547.7(2) 554.3(2)	$(\nu_6 + \nu_4) + 7\nu_4 - 7\nu_4$ $(\nu_6 + \nu_4) + 6\nu_4 - 6\nu_4$ $(\nu_6 + \nu_4) + 5\nu_4 - 5\nu_4$ $(\nu_6 + \nu_4) + 4\nu_4 - 4\nu_4$ $(\nu_6 + \nu_4) + 3\nu_4 - 3\nu_4$ $(\nu_6 + \nu_4) + 2\nu_4 - 2\nu_4$ $(\nu_6 + \nu_4) + \nu_4 - \nu_4$ $(\nu_6 + \nu_4)$	5(IR,G)	[a] $T = 203$ K; Q heads C-type bands
634.9	ν_{10} (?)	12(IR,S)	$T = 20$ K
676.8	ν_8	10(Ra,S)	See also 1(Ra,L); 6(Ra,S); 7(Ra,M)
676.6(2) 683.9(2) 689.5(2) 695.7(2) 701.8(2) 709.1(2)	$(\nu_3 + \nu_7) + n\nu_4 - n\nu_4$	14(IR,G)	[c] Q heads See also 5(IR,G) See also 5(IR,G)
708	$\nu_3 + \nu_7$ (?)	8(IR,LXe)	$T = 165$ K See also 1(IR,G)
744(1) P 751(1) Q 759(1) R	ν_{12} A-type band	5(IR,G)	[a] $T = 203$ K See also 1(IR,L + G); 2,3,9(IR,M);6,12(IR,S); $T = 203$ K See also 8(IR,LXe)

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
751.3(2)	ν_{12}^0	14(IR,G)	[b]
761(1)	$\nu_6+\nu_{10}$	5(IR,G)	[a] $T=203$ K See also 6(IR,S) Suggested to form a Fermi diad with ν_{12} In 12(IR,S), a similar band at 752.1 cm^{-1} is supposed to play the same role with $\nu=736.6$ cm^{-1}, but is attributed to $(\nu_{10}+\nu_{R3})$
811.7	ν_2	10(Ra,S)	See also 1,6(Ra,S); 1,11(Ra,L); 4,7(Ra,M)
1000	$\nu_3+\nu_{12}$	8(IR,LXe)	$T=165$ K
1004.6(2) 1011.1(2) 1017.8(2) 1036.4(2)	$(\nu_3+\nu_{12})+n\nu_4-n\nu_4$	14(IR,G)	[c] Q heads See also 5(IR,G)
1102.3(2)	$(\nu_7+\nu_8)^0$	14(IR,G)	[b] See also 8(IR,LXe)
1194.0(2) 1197.3(2) 1201.2(2) 1205.5(2) 1207.0(2) 1210.4(2) 1212.5(2) 1215.7(2) 1217.3(2) 1221.9(2) 1224.0(2) 1227.7(2) 1233.3(2)	$(\nu_2+\nu_7)+n\nu_4-n\nu_4$ (?)	14(IR,G)	[c]
1237	$\nu_2+\nu_7$ (?)	8(IR,LXe)	$T=165$ K
1256(1) P 1264(1) Q 1272(1) R	ν_{11} A-type band	5(IR,G)	[a] See also 1(IR,L+G); 2,3,9(IR,M); 6,12(IR,S); 8(IR,LXe) 8(IR,LXe)
1261.1(2)	ν_{11}^0	14(IR,G)	[b]
1335.5	$2\nu_8$	10(Ra,S)	See also 1(Ra,L); 1,6(Ra,S) Fermi resonance is suggested with ν_1
1382.3	ν_1	10(Ra,S)	See also 1,6(Ra,S); 1,11(Ra,L); 4,7(Ra,M)
1491.4(2)	$(\nu_9-\nu_3)^0$	14(IR,G)	[b] See also 1(IR,G); 8(IR,LXe)
1546	$\nu_2+\nu_{12}$	8(IR,LXe)	$T=165$ K See also 1(IR,L)
1681	$2\nu_8+\nu_{10}$ (?) or $\nu_3+\nu_8+\nu_{12}$ (?)	8(IR,LXe)	$T=165$ K See also 1(IR,L)
1723.5	ν_5	10(Ra,S)	See also 1(Ra,L); 1,6(Ra,S); 7(Ra,M)
1733(1)	$(\nu_1+\nu_{10})^0$ or $(\nu_6+\nu_{11})^0$	14(IR,G)	[b,d]

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
1752(1) P 1764(1) R	ν_9 B-type band	5(IR,G)	[a] $T=203$ K See also 1(IR,L+G); 2,3,9(IR,M); 6,12(IR,S); 8(IR,LXe) In 12(IR,S), the corresponding band at 1750.1 cm^{-1} is supposed to form a Fermi diad with a band at 1727.9 cm^{-1} attributed to $(\nu_6+\nu_{11})$; see also 8(IR,LXe) for the same observation
1756.7650(15)	ν_9^0	15(IR,G)	[d,e] See also 14(IR,G)
~1782	$\nu_4+\nu_5$	8(IR,LXe)	$T=165$ K
1802	$\nu_1+\nu_7$	8(IR,LXe)	$T=165$ K
1936.7(2)	$(\nu_8+\nu_{11})^0$	14(IR,G)	[b] See also 1(IR,G); 8(IR,LXe)
2004(1)	$(\nu_3+\nu_9)^0$	14(IR,G)	[b] See also 8(IR,LXe)
2063.0(2)	$(\nu_2+\nu_{11})^0$	14(IR,G)	[b] See also 8(IR,LXe)
2125(1)	$(\nu_1+\nu_{12})^0$ A-type band	14(IR,G)	[b] See also 1(IR,G); 8(IR,LXe)
2586.5(2)	$(2\nu_8+\nu_{11})^0$	14(IR,G)	[b] See also 1(IR,G); 8(IR,LXe)
2631.5(2)	$(\nu_1+\nu_{11})^0$ A-type band	14(IR,G)	[b] See also 1(IR,L+G); 8(IR,LXe)
2750.0(2)	$(\nu_{11}+2\nu_{12})^0$	14(IR,G)	[b] See also 1(IR,G)
2973.0(2)	$(\nu_5+\nu_{11})^0$ B-type band	14(IR,G)	[b] See also 1(IR,L+G); 8(IR,LXe)
3066(1)	$(2\nu_8+\nu_9)^0$ B-type band	14(IR,G)	[b] See also 8(IR,LXe)
3088	$\nu_1+\nu_6+\nu_{11}$	8(IR,LXe)	Possible Fermi resonance
3106	$\nu_1+\nu_9$	8(IR,LXe)	See also 1(IR,L+G)
3117(1)	$(\nu_1+\nu_9)^0$	14(IR,G)	[b]
3159(1)	$(2\nu_1+\nu_7)^0$	14(IR,G)	[b]
3241(1)	$(\nu_2+\nu_5+\nu_{12})^0$ or $(\nu_3+\nu_5+\nu_{11})^0$	14(IR,G)	[b]
3416.5	$\nu_5+\nu_6+\nu_{11}$	8(IR,LXe)	Possible Fermi resonance
3435	$\nu_5+\nu_9$	8(IR,LXe)	See also 1(IR,L+G)
3442(1)	$(\nu_5+\nu_9)^0$ A-type band	14(IR,G)	[b]
3773(1)	$(\nu_2+\nu_5+\nu_{11})^0$ B-type band	14(IR,G)	[b]
3910(?)	$\nu_1+\nu_2+\nu_9$ (?)	14(IR,G)	
3992(1)	$(2\nu_1+\nu_{11})^0$	14(IR,G)	[b]
4251(1)	$(\nu_9+2\nu_{11})^0$	14(IR,G)	[b] See also 1(IR,G)
4330(1)	$(\nu_1+\nu_5+\nu_{11})^0$ B-type band	14(IR,G)	[b]

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
4478(1)	$(2\nu_1+\nu_9)^0$	14(IR,G)	[b]
4668(1)	$(2\nu_5+\nu_{11})^0$	14(IR,G)	[b] See also 1(IR,G)
4802(1)	$(\nu_1+\nu_5+\nu_9)^0$	14(IR,G)	[b]
5118(1)	$(3\nu_9)^0$ or $(2\nu_5+\nu_9)^0$	14(IR,G)	[b] See also 1(IR,G)
6939(1)	$(2\nu_1+\nu_2+\nu_5+\nu_9)^0$	14(IR,G)	[b]

[a] Number in parentheses refers to the last quoted digits and represents the accuracy of line position measurements.

[b] Number in parentheses refers to the last quoted digits and represents the accuracy of band origin measurements.

[c] Number in parentheses refers to the last quoted digits and represents the accuracy of head measurements.

[d] Supersonic molecular beam experiment.

[e] Band origin calculated from rotational analysis; number in parenthesis refers to the last quoted digits and represents one standard deviation.

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4.7.b. *asym*-N_2O_4 : D-type

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	N=O stretch	1806	Ra : 4(M:Ne)
			1829	IR : 1(M:Ar,O_2); 3(M:O_2); 5(M:Ar)
			1850	Ra : 6(S)
			1861	IR : 2(M:N_2)
	ν_2	NO_2 a-stretch	1628	IR : 2(M:N_2)
			1635	Ra : 4(M:Ne)
			1645	IR : 1(M:Ar,O_2); 3(M:O_2); 5(M:Ar) Ra : 4(M:Xe)
	ν_3	NO_2 s-stretch	1279	IR : 2(M:N_2)
			1290	IR : 1(M:Ar,O_2); 3(M:O_2); 5(M:Ar)
			1295	Ra : 4(M:Ne)
			1300	Ra : 4(M:Xe); 6(S)
	ν_4	N–O stretch in O=N–O	904	IR : 1(M:O_2); 5(M:Ar)
			911	IR : 2(M:N_2)
	ν_5	NO_2 bend	783	IR : 1,3(M:O_2) Ra : 4(M:Ne)
			788	IR : 1,5(M:Ar) Ra : 4(M:Xe)
			792	IR : 2(M:N_2)
	ν_6	O=N–O bend	624	Ra : 4(M:Ne,Xe)
			641	IR : 1,3(M:O_2) Ra : 6,7(S)
			647	IR : 2(M:N_2)
A'	ν_7	NO_2 rock (in plane)	488	IR : 1(M:O_2) The authors suggest two possible assignments: ν_7 or ν_{10}
	ν_8	N–O–N bend	–	
	ν_9	N–O stretch in O–NO_2	–	
A"	ν_{10}	NO_2 wag (out of plane)	488	IR : 1(M:O_2) See remarks on ν_7
	ν_{11}	torsion	–	
	ν_{12}	torsion	–	

One extra band at 304 cm^{-1} was observed by Ref. 3 (IR,M:O_2); it was tentatively assigned to D-type N_2O_4. The band at 263 cm^{-1}, which was attributed to the ν_{10} mode of N_2O_4 with D_{2h} symmetry (see Ref. 6 (IR,S), in Sec. 4.7.a. *sym*-N_2O_4), has also been observed by Ref. 7 (Ra,S); the latter authors proposed that this band belongs to *D* or *D'*-type N_2O_4.

Observed Infrared Bands

Apart from the fundamental bands listed above, only one other band is mentioned by Ref. 1 (IR,M:O_2): $(\nu_2+\nu_7)$ or $(\nu_2+\nu_{10})$ at 2132 cm^{-1}.

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4.7.c. *asym*-N_2O_4 : D′-type

Besides the bands attributed to *D*-type N_2O_4, a few weak bands were observed and tentatively attributed to the *D*′-type by Ref. 1(IR,M:O_2). Four peaks have also been attributed by Ref. 2(IR,S) to this isomer. We list here the assignments. The discrepancy between the observations of the two groups of workers is attributed "to the floppiness of these molecular forms, the frequencies being very sensitive to the environment" (see Ref. 2(IR,S)). These assignments for the *D*′-type N_2O_4 obviously need further support.

Mode	Frequency (cm^{-1}) 1(IR,M:O_2)	 2(IR,S)
ν_1	1889–1899	2003
ν_2	1584	1542
ν_3	1290	1305
ν_4	916	959
ν_5	794	
ν_6	660	
ν_7 or ν_{10}	524	

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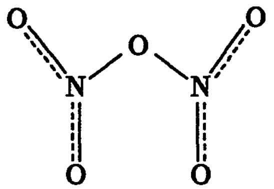
4.8. N_2O_5

The molecule is supposed to be planar, of C_{2v} symmetry, but electron diffraction measurements (6), analyzed using a dynamical model, suggest a C_2 structure.

Species	Molecular point group	Normal modes Symmetry	Vibrations	Activity Raman	Infrared
Planar					
	C_{2v}	A_1	$\nu_1 \rightarrow \nu_6$	A	A
		A_2	ν_7, ν_8	A	I
		B_1	ν_9, ν_{10}	A	A
		B_2	$\nu_{11} \rightarrow \nu_{15}$	A	A
Non planar					
	C_2	A	$\nu_1 \rightarrow \nu_8$	A	A
		B	$\nu_9 \rightarrow \nu_{15}$	A	A

Observed Fundamental Vibrational Frequenciea[a]

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A_1	ν_1	NO_2 a-stretch in phase	1716	9(G)
			1720	1,5(G)
			1728	2(G)
			1744	2(S); 3(M:N_2)
			1752	1(M:CO_2)
	ν_2	NO_2 s-stretch in phase	1300	4(M:O_2)
			1305	3(M:N_2)
			1316	1(M:CO_2)
			1337	2(G+S); 9(G)
	ν_3	NO_2 bend in phase	732	2(S)
			737	1(M:CO_2); 3(M:N_2); 4(M:O_2); 7(M:Ar)
			743	1,2,5,9(G)
	ν_4	NO_2 rock (in plane)	~600	2(S)
			~614	2(G)
	ν_5	N–O–N s-stretch	337	2(S)
			353	2,10(G)
	ν_6	N–O–N bend	~85	2(S); from combination bands
A_2	ν_7	NO_2 wag (out of plane)	–	
	ν_8	NO_2 s-twist	–	
B_1	ν_9	NO_2 wag (out of plane)	557	5(G)
			562	2(S)
			577	2(G)
	ν_{10}	NO_2 a-twist	~50	10(G)
B_2	ν_{11}	NO_2 a-stretch out of phase	1703	1(M:CO_2); 2(S); 3(M:N_2); 4(M:O_2); 7(M:Ar)
			1718	1,5,9(G)
			1728	2(G)
	ν_{12}	NO_2 s-stretch out of phase	1241	4(M:O_2)
			1246	1,2,5,9(G); 1(M:CO_2); 2(S); 3(M:N_2); 7(M:Ar)
	ν_{13}	N–O–N a-stretch	853	2(S)
			860	2,9(G)
	ν_{14}	NO_2 bend out of phase	712	2(S)
			719	1(M:CO_2)
			737	3(M:N_2); 4(M:O_2); 7(M:Ar)
			743	1,2,5,9(G)
	ν_{15}	NO_2 rock (in plane)	337	2(S)
			353	2,10(G)

[a] All the observations were made with infrared techniques.

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
50	ν_{10}	10(G)	
353	ν_5 or ν_{15}	2(G)	See also 2(S); 10(G)
439	$\nu_5+\nu_6$ (?)	2(G)	
577	ν_9	2(G)	See also 2(S); 5(G)
614	ν_4	2(G)	See also 2(S)
743.38 (2)	ν_3 or ν_{14}	5(G)	[a,b] Q head; R,Q,P structure See also 1,2,9(G); 1,3,4,7(M); 2(S)
860	ν_{13}	2,9(G)	See also 2(S)
986	(ν_1 or ν_{11})–(ν_3 or ν_{14}) (?)	2(G)	
1245.86(6)	ν_{12}	5(G)	[a,b] Q head; R,Q,P structure See also 1,2,9(G); 1,3,4,7(M); 2(S)
1338	ν_2	2(G)	See also 1,3,4(M); 2(S); 9(G)
1430	$\nu_2+\nu_6$ (?)	2(G)	
1720	ν_1 or ν_{11}	5(G)	[b] See also 1,2,9(G); 1,3,4,7(M); 2(S)
2072	(ν_1 or ν_{11}) + ν_5 (?)	2(G)	
2314	(ν_1 or ν_{11}) + ν_4 (?)	2(G)	
2574	$\nu_2+\nu_{12}$	2(G)	See also 5,9(G)
2954	(ν_1 or ν_{11}) + ν_{12}	2(G)	See also 5,9(G)
3053	(ν_1 or ν_{11}) + ν_2	2(G)	See also 5,9(G)
3424	$2\nu_1$ or $2\nu_{11}$	2(G)	
3528	($2\nu_1$ or $2\nu_{11}$) + ν_6	2(G)	

[a] Number in parentheses refers to the last quoted digits and represents the accuracy of line position measurements.

[b] Rotational line list available in ATMOS database[8].

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[6] B. W. McClelland, L. Hedberg, K. Hedberg, and K. Hagen, J. Am. Chem. Soc. **105**, 3789 (1983).

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[8] Molecular line parameters for the Atmospheric Trace MOlecular Spectroscopy experiment, L. R. Brown, C. B. Farmer, C. P. Rinsland, and R. A. Toth, Appl. Opt. **26**, 5154 (1987).

[9] C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, Chem. Phys. Lett. **148**, 358 (1988).

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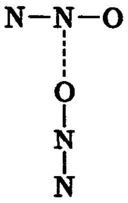
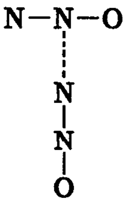
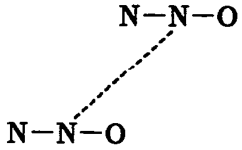
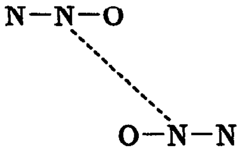
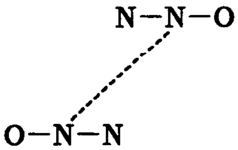
4.9. $(N_2O)_2$

Species	Molecular	Normal modes		Activity	
	point group	Symmetry	Vibrations	Raman	Infrared
(a)  (b)  (c) 	C_s	A'	$\upsilon_1 \rightarrow \upsilon_9$	A	A
		A''	$\upsilon_{10} \rightarrow \upsilon_{12}$	A	A
(a)  (b) 	C_{2h}	A_g	$\upsilon_1 \rightarrow \upsilon_5$	A	I
		A_u	υ_6, υ_7	I	A
		B_g	υ_8	A	I
		B_u	$\upsilon_9 \rightarrow \upsilon_{12}$	I	A

Observed Fundamental Vibrational Frequencies

The (a) species of C_{2h} symmetry is now the unique one recognized by several authors. No Raman experiment seems to be reported. Therefore, $\upsilon_1 \rightarrow \upsilon_5$ and υ_8 were not observed. On the other hand, to our knowledge, only two fundamental frequencies have been observed in infrared spectra. They correlate with the υ_1 (N–O stretch) and υ_3 (N–N stretch) of N_2O and are of B_u symmetry. We will call them υ_9 and υ_{10}.

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
B_u	ν_9	out of phase N–O stretch	1279.711	$\underline{4}$(IR,G)
	ν_{10}	out of phase N–N stretch	2229.48	1,$\underline{2}$(IR,G)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
1279.7107(6)	ν_9^0	4(IR,G)	[a] T_{rot} = 5–10 K
~1277.7 P 1279.7 Q ~1281.7 R	ν_9 (A,B)-type band	4(IR,G)	T_{rot} = 5–10 K
2229.48	ν_{10}	2(IR,G)	See also 1(IR,G)
3478.4357(30)	$(\nu_9+\nu_{10})^0$	3(IR,G)	[a]

[a] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents one standard deviation.

References

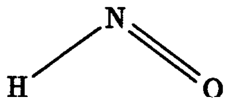
[1] T. E. Gough, R. E. Miller, and G. Scoles, J. Chem. Phys. **69**, 1588 (1978).

[2] B. J. Howard, 42nd Symposium on Molecular Spectroscopy, Columbus Ohio (1987), WA2.

[3] Z. S. Huang and R. E. Miller, J. Chem. Phys. **89**, 5408 (1988).

[4] Y. Ohshima, Y. Matsumoto, M. Takami, and K. Kuchitsu, Chem. Phys. Lett. **152**, 294 (1988).

4.10. HNO

Species	Molecular point group	Normal modes Symmetry	 Vibrations	Activity Raman	 Infrared
	C_s	A'	$\nu_1 \rightarrow \nu_3$	A	A

Useful information on the structure of this molecule is presented in Ref. 3.

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	N–H stretch	2683.9521	2,6,7(IR,G)
			2716	4(IR,M:Ar)
			2756	4(IR,M:N_2)
	ν_2	bend	1500.819	2,6(IR,G); 5(LSS,G)
			1505	4(IR,M:Ar)
			1511	4(IR,M:N_2)
	ν_3	N=O stretch	1565.348	2,6(IR,G); 4(IR,M:Ar); 5(LSS,G)
			1568.5	1(IR,M:Ar); 4(IR,M:N_2)

Observed Infrared Bands

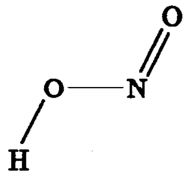
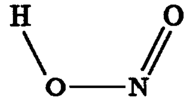
Frequency (cm^{-1})	Assignment	References	Remarks
1500.8192(14)	ν_2^0	5(LSS,G)	[a]
	(A,B)-type band	6(IR,G)	Coriolis interaction with ν_3 See also 2(IR,G); 4(IR,M)
1565.3481(4)	ν_3^0	5(LSS,G)	[a]
	(A,B)-type band	6(IR,G)	Coriolis interaction with ν_2 See also 1,4(IR,M); 2(IR,G)
2665.3	$2\nu_1-\nu_1$	2(IR,G)	
2683.95210(8)	ν_1^0	6,7(IR,G)	[a]
	(A,B)-type band		See also 2(IR,G); 4(IR,M)
~3300	$2\nu_3$ ou $\nu_2+\nu_3$ (?)	1(IR,M:Ar)	$T=20$ K

[a] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents one standard deviation.

References

[1] H. W. Brown and G. C. Pimentel, J. Chem. Phys. **29**, 883 (1958).
[2] P. N. Clough, B. A. Thrush, D. A. Ramsay, and J. G. Stamper, Chem. Phys. Lett. **23**, 155 (1973).
[3] S. Saito and K. Takagi, J. Mol. Spectrosc. **47**, 99 (1973).
[4] M. E. Jacox and D. E. Milligan, J. Mol. Spectrosc. **48**, 536 (1973).
[5] J. W. C. Johns and A. R. W. McKellar, J. Chem. Phys. **66**, 1217 (1977).
[6] J. W. C. Johns, A. R. W. McKellar, and E. Weinberger, Can. J. Phys. **61**, 1106 (1983).
[7] J. C. Petersen and M. Vervloet, Chem. Phys. Lett. **141**, 499 (1987).

4.11. HNO_2

Species	Molecular point group	Normal modes Symmetry	 Vibrations	Activity Raman	 Infrared
trans-HONO 	C_s	A'	$\nu_1 \rightarrow \nu_5$	A	A
		A''	ν_6	A	A
cis-HONO 	C_s	A'	$\nu_1 \rightarrow \nu_5$	A	A
		A''	ν_6	A	A

4.11.a. *trans*-HONO

This species is the most stable one.

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	O–H stretch	3512	4(IR,S)
			3558	3(IR,M:N_2)
			3590.770	1,2,4,7,8,10,15(IR,G)
	ν_2	N=O stretch	1635	4(IR,S)
			1687	3(IR,M:N_2); 5,14(IR,M:Ar)
			1699.758	1,2,4,7,8,10,18(IR,G); 6(LSS,G); 9(DL,G)
	ν_3	H–O–N bend	1421	4(IR,S)
			1298	3(IR,M:N_2)
			1263.2069	1,2,4,7,8,10,18(IR,G); 5(IR,M:Ar); 13(DL,G)
	ν_4	O–N stretch	790.1170	1,2,4,7,8,10,11,17(IR,G)
			795	14(IR,M:Ar)
			801	4(IR,S); 5(IR,M:Ar)
			815	3(IR,M:N_2)
	ν_5	O–N–O bend	595.620	1,2,4,8,10,11(IR,G)
			625	3(IR,M:N_2)
			702	4(IR,S)
A''	ν_6	torsion	499	4(IR,S)
			543.880	1,2,4,8,10,11(IR,G)
			550	5(IR,M:Ar)
			583	3(IR,M:N_2)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
543.880(4)	v_6^0	11(IR,G)	[b,c] Global fit with v_5 band rotational data, taking into account a Coriolis interaction between v_5 and v_6 levels. See also 8(IR,G)
540	v_6 C-type band	4(IR,G)	Q head See also 1,2,10(IR,G); 3,5(IR,M); 4(IR,S)
595.620(5)	v_5^0	11(IR,G)	[b,c] Global fit with v_6 band rotational data, taking into account a Coriolis interaction between v_5 and v_6 levels. See also 8(IR,G)
580 P 593 Q 607 R	v_5 A-type band	4(IR,G)	See also 1,2,10(IR,G); 3(IR,M); 4(IR,S)
790.117045(32)	v_4^0	17(IR,G)	[a,c,e] See also 8,11(IR,G)
777 P 791 Q 806 R	v_4 A-type band	4(IR,G)	See also 1,2,7,10(IR,G); 3,5,14(IR,M); 4(IR,S)
1263.20693(5)	v_3^0	18(IR,G)	[a,c,e] See also 8(IR,G); 13(DL,G)
1252 P 1265 Q 1278 R	v_3 (A,b)-type band	4(IR,G)	Perturbations due to resonance with $2v_5$ and v_4+v_6 See also 1,2,7,10,18(IR,G); 3,5(IR,M); 4(IR,S)
1699.7582(6)	v_2^0	9(DL,G)	[a,c,e] See also 6(LSS,G); 8,18(IR,G)
1684 P 1699 Q 1715 R	v_2 (A,b)-type band	4(IR,G)	Perturbations due to resonance with v_5+2v_6 and $2v_5+v_6$ See also 1,2,7,10,18(IR,G); 3,5,14(IR,M); 4(IR,S)
3372.12(6)	$2v_2^0$	8(IR,G)	[a,d] See also 18(IR,G)
3360 P 3372 Q 3392 R	$2v_2$ A-type band	4(IR,G)	See also 1,7,18(IR,G)
3590.77022(13)	v_1^0	15(IR,G)	[a,c,e] See also 8(IR,G)
3575 P 3588 Q 3605 R	v_1 (A,b)-type band	4(IR,G)	Coriolis interaction with $2v_3+v_5+v_6$ See also 1,2,7,10(IR,G); 3(IR,M); 4(IR,S)
4124	v_2+2v_3 A-type band	1(IR,G)	
4378.3	$(v_1+v_4)^0$ (A,B)-type band	18(IR,G)	See also 1,16(IR,G)

Observed Infrared Bands – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
4829.6	$(\nu_1+\nu_3)^0$ A-type band	18(IR,G)	See also 1(IR,G)
5038	$3\nu_2^0$ (?)	1(IR,G)	
6045.4	$(\nu_1+2\nu_3)^0$ A-type band	18(IR,G)	See also 1(IR,G)
7016.78895(20)	$2\nu_1^0$ (A,b)-type band	18(IR,G)	[a,c] See also 1,16(IR,G)
10280.483(11)	$3\nu_1^0$ (A,b)-type band	18(IR,G)	[a,c] See also 16(IR,G); possible resonance with $2\nu_1+\nu_2+2\nu_4$
13385	$4\nu_1^0$ (A,b)-type band	16(IR,G)	Possible resonance with $3\nu_1+2\nu_3+\nu_5$

[a] Number in parentheses refers to the last quoted digits and represents one standard deviation.

[b] Number in parentheses refers to the last quoted digits and represents the absolute accuracy of line position measurements.

[c] Band origin calculated from rotational analysis.

[d] Band origin calculated from band shape simulation.

[e] Rotational line list available in ATMOS database (12).

References

[1] L. H. Jones, R. M. Badger, and G. E. Moore, J. Chem. Phys. 19, 1599 (1951).

[2] L. D'Or and P. Tarte, Bull. Soc. Roy. Sci. Liège 20, 478 (1951).

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[5] W. A. Guillory and C. E. Hunter, J. Chem. Phys. 54, 598 (1971).

[6] M. Allegrini, J. W. C. Johns, A. R. W. McKellar, and P. Pinson, J. Mol. Spectrosc. 79, 446 (1980).

[7] R. H. Kagann and A. G. Maki, J. Quant. Spectrosc. Radiat. Transfer 30, 37 (1983).

[8] C. M. Deeley and I. M. Mills, J. Mol. Struct. 100, 199 (1983).

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[10] C. M. Deeley and I. M. Mills, Mol. Phys. 54, 23 (1985).

[11] C. M. Deeley, I. M. Mills, L. O. Halonen, and J. Kauppinen, Can. J. Phys. 63, 962 (1985).

[12] Molecular line parameters for the Atmospheric Trace MOlecule Spectroscopy experiment, L. R. Brown, C. B. Farmer, C. P. Rinsland, and R. A. Toth, Appl. Opt. 26, 5154 (1987).

[13] A. G. Maki, J. Mol. Spectrosc. 127, 104 (1988).

[14] J. N. Crowley and J. R. Sodeau, J. Phys. Chem. 93, 4785 (1989).

[15] J.-M. Guilmot, M. Carleer, M. Godefroid, and M. Herman, J. Mol. Spectrosc. 143, 81 (1990).

[16] S. M. Holland, R. J. Stickland, M. N. R. Ashfold, D. A. Newnham, and I. M. Mills, J. Chem. Soc. Faraday Trans. 87, 3461 (1991).

[17] I. Kleiner, J.-M. Guilmot, M. Carleer, and M. Herman, J. Mol. Spectrosc. 149, 341 (1991).

[18] J.-M. Guilmot and M. Herman, To be published (1992).

4.11.b. *cis*-HONO

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	O–H stretch	3411	3(IR,M:N$_2$); 5(IR,M:Ar)
			3426.193	1,2,4,7,8,10,$\underline{17}$(IR,G)
	ν_2	N=O stretch	1611	4(IR,S)
			1628	1(IR,G)
			1633	3(M:N$_2$); 5,13(IR,M:Ar)
			1640.517	2,4,7(IR,G); $\underline{6}$(LSS,G)
	ν_3	H–O–N bend	1261	4(IR,G); 5,13(IR,M:Ar)
	ν_4	O–N stretch	851.9431	4,7,8,10,11,$\underline{15}$(IR,G); 5,13(IR,M:Ar); 9(DL,G)
			857	1,2(IR,G); 4(IR,S)
			865	3(IR,M:N$_2$)
	ν_5	O–N–O bend	609	4,$\underline{8}$(IR,G); 5,13(IR,M:Ar)
			721	4(IR,S)
A''	ν_6	torsion	518	4(IR,S)
			639	1,2,4,$\underline{8}$(IR,G); 5,13(IR,M:Ar)
			658	3(IR,M:N$_2$)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
609.0(5)	ν_5^0	8(IR,G)	[a,c]
608	ν_5	4(IR,G)	Q head See also 4(IR,S); 5,13(IR,M)
638.5(5)	ν_6^0	8(IR,G)	[a,c]
638	ν_6 C-type band	4(IR,G)	Q head See also 1,2(IR,G); 3,5,13(IR,M); 4(IR,S)
851.943054(32)	ν_4^0	15(IR,G)	[a,b,d] See also 8,10,11(IR,G); 9(DL,G)
842 P 853 Q 868 R	ν_4 (A,b)-type band	4(IR,G)	See also 1,2,7(IR,G); 3,5,13(IR,M); 4(IR,S)
1261	ν_3 A-type band	4(IR,G)	Q head See also 5,13(IR,M)
1640.517(1)	ν_2^0	6(LSS,G)	[a,b,d]
1640	ν_2 (A,b)-type band	4(IR,G)	Q head See also 1,2,7(IR,G); 3,5,13(IR,M); 4(IR,S)
2493.00(5)	$(\nu_2+\nu_4)^0$	8(IR,G)	[a,c] See also 1,7,16(IR,G)
3257.98(8)	$2\nu_2^0$ A-type band	8(IR,G)	[a,c] See also 1,7,16(IR,G)
3426.19275(40)	ν_1^0 (a,B)-type band	17(IR,G)	[a,b] See also 1,2,4,7,8,10(IR,G); 3,5(IR,M)

Observed Infrared Band – Continued

Frequency (cm^{-1})	Assignment	References	Remarks
4281	$(\upsilon_1+\upsilon_4)^0$ (A,B)-type band	14,16(IR,G)	
4829	$3\upsilon_2^0$ (A,b)-type band	14(IR,G)	Reassigned by 16(IR,G) to $(\upsilon_1+\upsilon_3)^0$ for *trans*-HNO$_2$
6664.5	$2\upsilon_1^0$ (a,B)-type band	16(IR,G)	See also 1,14(IR,G)

[a] Number in parentheses refers to the last quoted digits and represents one standard deviation.
[b] Band origin calculated from rotational analysis.
[c] Band origin calculated from band shape simulation.
[d] Rotational line list available in ATMOS database (12).

References

[1] L. H. Jones, R. M. Badger, and G. E. Moore, J. Chem. Phys. 19, 1599 (1951).
[2] L. D'Or and P. Tarte, Bull. Soc. Roy. Sci. Liège 20, 478 (1951).
[3] R. T. Hall and G. C. Pimentel, J. Chem. Phys. 38, 1889 (1963).
[4] G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, J. Chem. Phys. 45, 1392 (1966).
[5] W. A. Guillory and C. E. Hunter, J. Chem. Phys. 54, 598 (1971).
[6] M. Allegrini, J. W. C. Johns, A. R. W. McKellar, and P. Pinson, J. Mol. Spectrosc. 79, 446 (1980).
[7] R. H. Kagann and A. G. Maki, J. Quant. Spectrosc. Radiat. Transfer 30, 37 (1983).
[8] C. M. Deeley and I. M. Mills, J. Mol. Struct. 100, 199 (1983).
[9] A. G. Maki and R. L. Sams, J. Mol. Struct. 100, 215 (1983).
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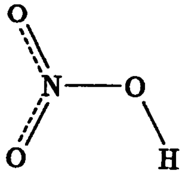
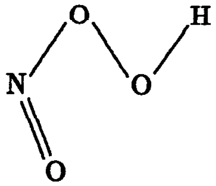
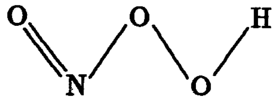
[11] C. M. Deeley, I. M. Mills, L. O. Halonen, and J. Kauppinen, Can. J. Phys. 63, 962 (1985).
[12] Molecular line parameters for the Atmospheric Trace MOlecule Spectroscopy experiment, L. R. Brown, C. B. Farmer, C. P. Rinsland, and R. A. Toth, Appl. Opt. 26, 5154 (1987).
[13] J. N. Crowley and J. R. Sodeau, J. Phys. Chem. 93, 4785 (1989).
[14] S. M. Holland, R. J. Stickland, M. N. R. Ashfold, D. A. Newnham, and I. M. Mills, J. Chem. Soc. Faraday Trans. 87, 3461 (1991).
[15] I. Kleiner, J. -M. Guilmot, M. Carleer, and M. Herman, J. Mol. Spectrosc. 149, 341 (1991).
[16] J.-M. Guilmot and M. Herman, To be published (1992).
[17] J.-M. Guilmot, F. Mélen, and M. Herman, To be published (1992).

4.12. HNO$_3$

Species	Molecular point group	Normal modes		Activity	
		Symmetry	Vibrations	Raman	Infrared
Nitric acid (HONO$_2$) 	C$_s$	A'	$\upsilon_1 \rightarrow \upsilon_7$	A	A
		A''	υ_8, υ_9	A	A
Peroxynitrous acid (HOONO) *cis*  *trans* 		For the HOONO species, the O–H bond is nearly perpendicular to the O=N–O plane. These two molecular species are then non planar, and have no symmetry element.			

4.12.a. Nitric acid ($HONO_2$)

Observed Fundamental Vibrational Frequencies

Sym.	Mode	Approximate type	Frequency (cm^{-1})	References, Remarks
A'	ν_1	O–H stretch	3106	3(IR,S)
			3400	1(Ra,L)
			3410	3(Ra,L)
			3520	15(IR,M:Ar)
			3550	3(IR,G)
			3560	2(IR,G)
	ν_2	NO_2 a-stretch	1646	3(IR,S)
			1675	1,3(Ra,L)
			1698	15(IR,M:Ar)
			1709.568	2,3(IR,G); 5,10(DL,G)
	ν_3	NO_2 s-stretch	1256	3(IR,S)
			1300	1,3(Ra,L)
			1320	15(IR,M:Ar)
			1325.735	2,3,14(IR,G); 7(LSS,G)
	ν_4	H–O–N bend	1303.518	3,14(IR,G); 15(IR,M:Ar)
			1395 (?)	3(Ra,L)
			1420 (?)	3(IR,S)
	ν_5	NO_2 bend (in plane)	879.108	2,3(IR,G); 6(DL,G)
			889.5	15(IR,M:Ar)
			896.9	
			925	1,3(Ra,L)
			958	3(IR,S)
	ν_6	O–NO_2 stretch	646.826	3,12(IR,G)
			680	1,3(Ra,L)
			722	3(IR,S)
	ν_7	O–NO_2 bend	580.304	2,3,12(IR,G)
			610	1,3(Ra,L)
			707	3(IR,S)
A''	ν_8	NO_2 bend (out of plane)	763.154	2,3,12(IR,G); 15(IR,M:Ar)
			769	1,3(Ra,L); estimated from $2\nu_8$ measurement
			773	3(IR,S)
	ν_9	O–H torsion	458.229	2,3,4,11(IR,G)
			483	3(Ra,L)

Observed Infrared Bands

Frequency (cm^{-1})	Assignment	References	Remarks
376.5	$6\nu_9-5\nu_9$	4(IR,G)	Q head
392.8	$5\nu_9-4\nu_9$	4(IR,G)	Q head
410.5	$4\nu_9-3\nu_9$	4(IR,G)	Q head; see also 3(IR,G)
422.1	$3\nu_9-2\nu_9$	4(IR,G)	Q head; see also 3(IR,G)
438.5	$2\nu_9-\nu_9$	4(IR,G)	Q head; see also 3(IR,G)
458.2287(5)	ν_9^0	11(IR,G)	[a]
457.8 Q	ν_9	4(IR,G)	See also 2(IR,G); 3(Ra,L)
475.0 R	C-type band	3(IR,G)	
580.3035(5)	ν_7^0	12(IR,G)	[a]
561.0 P	ν_7	3(IR,G)	See also 1,3(Ra,L);
579.0 Q			2(IR,G); 3(IR,S)
590.2 R	(A,b)-type band		
641.3	$\nu_6+\nu_9-\nu_9$	3(IR,G)	
646.8262(5)	ν_6^0	12(IR,G)	[a]
634.0 P	ν_6	3(IR,G)	See also 1,3(Ra,L);
646.6 Q			3(IR,S)
657.2 R	A-type band		
747.0	$\nu_8+\nu_9-\nu_9$	3(IR,G)	
763.1542(5)	ν_8^0	12(IR,G)	[a]
745.0 P	ν_8	3(IR,G)	See also 1,3(Ra,L);
762.2 Q			2(IR,G); 3(IR,S); 15(IR,M)
783.2	R C-type band		
879.1082(5)	ν_5^0	6(DL,G)	[a,b,c]
869.4 P	ν_5	3(IR,G)	Fermi resonance with $2\nu_9$
878.6 Q	A- or (A,b)-type band		See also 1,3(Ra,L); 2(IR,G); 3(IR,S); 15(IR,M)
896.4187	$2\nu_9^0$	8,9	Calculated line positions See also 3(IR,G); 15(IR,M) Fermi resonance with ν_5
845–909	$3\nu_9-\nu_9$	8	Calculated line positions
847–905	$\nu_5+\nu_9-\nu_9$	8	Calculated line positions
1033	$\nu_7+\nu_9$	3(IR,G)	
1099	$\nu_6+\nu_9$	3(IR,G)	
1205.7070(5)	$(\nu_8+\nu_9)^0$	13(IR,G)	[a]
	A-type band		See also 2,3(IR,G); 3(IR,S); 15(IR,M) Interaction with $\nu_6+\nu_7$
1218	$\nu_6+\nu_7$	3(IR,G)	Interaction with $\nu_8+\nu_9$
1303.5183(15)	ν_4^0	14(IR,G)	[a,b,d]
	(A,B)-type band		See also 3(IR,G+S); 3(Ra,L); 15(IR,M)
1311	P ν_3	3(IR,G)	See also 1,3(Ra,L);
1324.9	Q A- or (A,b)-type band		2(IR,G); 3(IR,S); 15(IR,M)

Observed Infrared Bands — Continued

Frequency (cm^{-1})	Assignment	References	Remarks
1325.7354(10)	ν_3^0	14(IR,G)	[a,b,d] See also 7(LSS,G)
1330.7	$\nu_5+\nu_9$ (?)	3(IR,G)	See also 2(IR,G); 3(Ra,L); 3(IR,S)
1380.3	$\nu_7+\nu_8$ (?)	15(IR,M:Ar)	$T=12$ K
1455	$\nu_5+\nu_7$	3(IR,G)	
1470	$\nu_7+\nu_8$	3(IR,S)	$T=85$ K
1515	$2\nu_8$	3(IR,G)	See also 1,3(Ra,L); 3(IR,S)
1521	$\nu_5+\nu_6$	3(IR,G)	
1709.5675(5)	ν_2^0	5,10(DL,G)	[a,b,c]
1693.0 P 1705.6 Q 1711.8 Q 1720.0 R	ν_2 B- or (a,B)-type band	3(IR,G)	See also 1,3(Ra,L); 2(IR,G); 3(IR,S); 15(IR,M)
1787	$\nu_3+\nu_9$	3(IR,G)	See also 15(IR,M)
1905	$2\nu_5$	3(IR,S)	$T=85$ K
2038	$\nu_4+\nu_8$	3(IR,S)	$T=85$ K
2163	$\nu_2+\nu_9$	3(IR,G)	
2194	$\nu_3+\nu_5$	3(IR,G)	
2200	$\nu_4+\nu_5$	3(IR,S)	$T=85$ K
2290	$\nu_2+\nu_4$	3(IR,S)	$T=85$ K
2585	$\nu_2+\nu_5$	2(IR,G)	See also 15(IR,M)
2632	$2\nu_4$	3(IR,G)	See also 2(IR,G)
2643	$\nu_3+\nu_4$	3(IR,G)	
2656	$2\nu_3$	3(IR,G)	See also 15(IR,M)
2999	$\nu_2+\nu_3$ or $\nu_2+\nu_4$	3(IR,G)	See also 2(IR,G); 15(IR,M)
3093	$\nu_1-\nu_9$	3(IR,G)	
3400	$2\nu_2$	3(IR,G)	See also 2(IR,G)
3538.0 P 3550.0 Q 3562.0 R	ν_1	3(IR,G)	See also 1,3(Ra,L); 2(IR,G); 3(IR,S); 15(IR,M)
3967.0	$\nu_1+\nu_9$	15(IR,M:Ar)	$T=12$ K

[a] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents the absolute accuracy of line position measurements.

[b] Rotational line list available in HITRAN database (8).

[c] Rotational line list available in ATMOS database (9).

[d] The origins as well as the rotational parameters were calculated taking into account Fermi and Coriolis interactions between ν_3 and ν_4; other perturbations due to unknown levels were also observed.

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4.12.b. *cis*-HOONO

Observed Fundamental Vibrational Frequencies

This species is supposed to be the most stable of the HOONO species. Five of the nine normal modes have been observed by Ref. 2(IR,M:Ar,N_2), and attributed by comparison with calculations (1). No other infrared band seems to be reported.

Approximate type	Observations (cm^{-1}) Frequency	Medium	Calculations (cm^{-1})
O–H stretch	3541.7 3545.5	N_2 Ar	3677
N=O stretch	1701.4 1703.6	N_2 Ar	1692
H–O–O bend	1364.4 1394.9	Ar N_2	1398
O–O stretch	952.0 960.5	Ar N_2	946
O–N=O bend	772.8 793.6	Ar N_2	814
O–N stretch	–		439
O–N=O torsion O–O–N bend [a]			384 337
H–O–O torsion	–		211

[a] According to Ref. 1, these two modes are coupled and cannot be exclusively assigned.

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4.12.c. *trans*-HOONO

Observed Fundamental Vibrational Frequencies

Five frequencies observed by Ref. 1(IR,M:Ar) have been assigned as fundamental modes of this species.

Approximate type	Frequency (cm^{-1})
O–H stretch	3563.3
N=O stretch	1708.3
H–O–O bend	1372.7
O–O stretch	957.4
O–N=O bend	782.9

Reference

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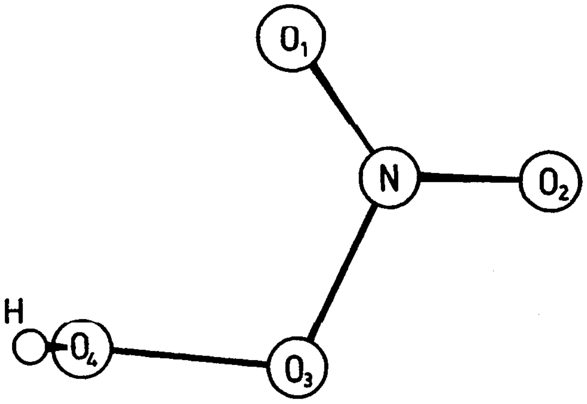
4.13. HNO_4 (HO_2NO_2)

The molecule is supposed to be non planar, and thus to have no symmetry element. The O_3 atom is nearly coplanar with O_1–N–O_2; the O_4 atom is below the plane, and the H atom is above the plane (see Ref. 5).



Observed Fundamental Vibrational Frequencies

Seven of the twelve normal modes have been observed and assigned by comparison with calculations. Two weak bands at 722 and 919 cm^{-1} have been observed by Ref. 8 (IR,G). They have been attributed to combination or hot bands of HNO_4, since the fundamental frequencies which remain unknown are supposed to lie at lower energies.

Approximate type (Following (4))	Observations (cm^{-1})		Calculations (cm^{-1})		
	Frequency	References, Remarks	(4)	(5)	
O–NO_2 torsion	~145	6(MW,G)	125	117	145
HO–O torsion	–		200	285	302
O–O–H bend	–		400	391	436
NO_2 rock	–		500	592	652
N–O stretch	–		633	727	821
NO_2 wag	–		735	810	896
NO_3	802.56(5)	[a,b] 9(IR,G) Band called υ_6 by 9(IR,G)		922	1046
	802.7	[c] 1,2,3(IR,G)			
O–O stretch	940	8(IR,G)	880	1050	1215
NO_3	1304.2	[c] 1,2,3(IR,G)		1405	1576
O–H bend	1396.9	[c] 1,2,3,9(IR,G) Band called υ_3 by 9(IR,G)		1540	1615
NO_3	1728.3	[c] 1,2,3(IR,G)		1705	1960
O–H stretch	3540.1	[c] 1,3(IR,G)		3910	4100

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[a] Rotational line list available in ATMOS database (7).

[b] Band origin calculated from rotational analysis; number in parentheses refers to the last quoted digits and represents the absolute accuracy of line position measurements.

[c] Q branch appears as a doublet; the value refers to the mean calculated from the positions of the two peaks.

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