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On the structure and the antisymmetric ν_3 IR mode of covalent azide group

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HIGHLIGHTS

- ▶ The IR stretching ν_3 mode frequency and the bond length asymmetry are correlated in organic and inorganic azides.
- ▶ An analytical expression as $\nu_3 = 1997 + 1.17 \times 10^3\ \Delta r$ with $R = 0.972$ is gained on the database of more than fifty azides.
- ▶ The blue shift $\Delta\nu_3$ from the free azide value varies in direct proportion with the N_3 group asymmetry.

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ABSTRACT

A new correlation $\nu_3 = 1997 + 1.17 \times 10^3\ \Delta r$ between the stretching mode ν_3 of the IR band frequency and the bond length asymmetry expressed as $\Delta r \equiv r(N_\alpha - N_\beta) - r(N_\beta - N_\gamma)$ is established in molecular azides $R{-}N_\alpha{-}N_\beta{-}N_\gamma$ with the correlation coefficient $R = 0.972$. The database represents recent spectral and structural information for more than fifty organic molecules and inorganic metal complexes. Because the absolute term practically coincides with the ν_3 frequency value for the free azide group, this correlation shows that the blue shift $\Delta\nu_3$ (in cm^{-1}) of the ν_3 from the free azide value varies in direct proportion with the N_3 group asymmetry Δr (in Å) ($\Delta\nu_3 = 1.17 \times 10^3\ \Delta r$) at formation of different azide structures.

1. Introduction

Organic and inorganic azides have been widely used in a number of areas of chemistry from organic synthesis and biology to industrial as explosive or propellants. A number of theoretical and experimental studies are published which include simple inorganic ionic azides, simple covalent organic azides and quite complicated organic complexes of different metals, which can contain both ionic and covalent azide groups. The chemistry and properties of these energetic organic and inorganic materials are discussed in detail in several relatively recent reviews [1–3]. The numerous studies of individual azide system are published and some are quoted in this communication.

Along with crystallography, NMR, and electron diffraction structural methods the molecular spectroscopy, infrared and Raman, is widely used in azide studies in condensed state. The analytical and structural application of infrared spectroscopy of azide complexes is based on the fact that tri-atomic azide group has very strong antisymmetric (ν_3) stretching vibrational mode band in the range of spectra ca. 2000–2200 cm^{-1}. If the symmetry of N_3 group is broken, the violation of the selection rule activates the symmetric (ν_1) stretching mode, which can also be seen in IR spectra around 1300–1350 cm^{-1}. The latter, however, is usually essentially weaker and can overlap with skeletal bands of complex counterion.

As reported previously, the azide ion is linear and symmetrical [4]. The covalently bonded azides mostly have a slightly bent unit and in all cases feature two distinctly different N_α–N_β and N_β–N_γ distances with asymmetry Δr, which can reach of 0.2 Å in N_5^+ ion [5].

As generally accepted the shift of the IR ν_3 band in different azide structures reflects the ionicity change of azide group [6]. The analysis of computed and observed frequency splitting is used for determination of crystal symmetry in cases when the study of single crystal is impossible [7].

Computations qualitatively confirmed this structural asymmetry and can predict approximate (but overestimated ca. 100 cm^{-1}) the frequency of the ν_{as} band [8] but correlation between these two – spectral and structural – quantities was never predict theoretically.

2. Experimental data

In gaseous free azide ions and in the nitrogen matrix, the ν_3 mode's frequency is 1986.5 cm^{-1} [9] and 2003.5 cm^{-1} [10]

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Table 1
Infrared v_3 frequencies and asymmetry $\Delta r \equiv r(N_\alpha - N_\beta) - r(N_\beta - N_\gamma)$ of azide $R{-}N_\alpha{-}N_\beta{-}N_\gamma$ groups.

No.	Frequency (cm^{-1})	Δr (Å)	Crystal	References
1	2004	1E-3	1,2-Bis-(dimethylamino)-N,N,N,N-tetramethyl-1,2-ethyldiaminium Azide	[22]
2	2003	0.012	$[(C_6H_5)_4]_3[Bi(N_3)_6]$	[6]
3	1983	0.014	$[Ph_4P]N_3$	[23]
4	2016	0.018	$[PNP]_2[Bi(N_3)_5]$	[6]
5	2025	0.027	$(bipy)_2Bi(N_3)_3]$	[6]
6	2028	0.03	$[P(C_6H_5)_4]_2[bipy\text{-}Bi(N_3)_5]$	[6]
7	2044	0.039	$[P(C_6H_5)_4]_2[bipy\text{-}Bi(N_3)_5]$	[6]
8	2049	0.039	$(bipy)_2Bi(N_3)_3]_2$	[6]
9	2061	0.042	$[P(C_6H_5)_4]_3[Bi(N_3)_6$	[6]
10	2039	0.045	Cadmium(II)ethylenediamine azide, $[Cd(en)(N_3)_2]L$.	[24]
11	2038	0.048	$[Ph_4Sb]N_3$	[23]
12	2063	0.053	$P(C_6H_5)_4]_2[bi\text{-}py]Bi(N_3)$	[23]
13	2077	0.054	$[PNP]_2[Bi(N_3)]$	[23]
14	2061	0.054	$[PPh_4]_2Ti(N_3)_6$	[25]
15	2073	0.057	$Zn(N_3)_2$[amino pyrazine]2$\{C_8H_{10}N_{12}Zn\}$	[26]
16	2079	0.065	$AgN_3{\cdot}2AgNO_3$	[27]
17	2106	0.072	$CH_3(N_3)$	[16]
18	2098	0.084	$\{Zn_2(N_3)_4$(py-tetrazole)$_2$(py-tetrazole)}	[28]
19	2080	0.087	$W(N_3)_6$.	[7]
20	2118	0.095	$\{Zn_2(N_3)_4$(py-tetrazole)2(py-tetrazole)	[28]
21	2113	0.097	$[(PPh_3)_2N]^+[P(N_3)_6]^-$	[29]
22	2100	0.098	$CH_2{=}CHCH_2(N_3)$	[16]
23	2133	0.098	$CH_3C{\equiv}CCH_2(N_3)$	[16]
24	2124	0.101	$CH_2{=}C(N_3)C(N_3){=}CH_2$	[16]
25	2135	0.101	$W(N_3)_6$	[7]
26	2103	0.102	$Sb(N_3)$	[30]
27	2123	0.102	1,3-Diazido-2- (azido methyl)-2-propyl amm. salts.,	[31]
28	2110	0.104	Bis(2-azidoethyl)ammonium Nitrocyanamide	[22]
29	2106	0.109	$As(N_3)$	[30]
30	2140	0.109	HN_3	[16]
31	2111	0.110	$CH_2{=}C(N_3)CH{=}CH_2$	[16]
32	2115	0.110	$N{\equiv}CCH_2(N_3)$	[16]
33	2123	0.112	$HC{\equiv}CH_2(N_3)$	[16]
34	2137	0.117	$CH_3CO(N_3)$	[16]
35	2132	0.121	Hydrazo-and Azo-1,3,5-triazine	[32]
36	2139	0.124	Hydroxylammonium azidotetrazolate-2-oxide	[33]
37	2156	0.126	1-Amino-5-azidotetrazole	[34]
38	2147	0.129	Hydrazinium 5-azidotetrazolate (CN_7^- anion)	[35]
39	2155	0.131	3,6-Di(azido)-1,2,4,5-tetrazine	[36]
40	2143	0.134	Potassium azidotetrazolate 2-oxide	[33]
41	2139	0.135	Hydroxylammonium azidotetrazolate 2-oxide	[33]
42	2165	0.140	Tetrazolyl azide, CHN7,	[37]
43	2152	0.142	1-(Aminoazidocarbamoyl)-5-azido tetrazol	[34]
44	2133	0.142	5-Azido-1-diazidocarbamoyl tetrazol	[34]
45	2172	0.143	Hydrazo-and Azo-1,3,5-triazine	[32]
46	2155	0.146	5-Azido-1-diazidocarbamoyl tetrazol	[34]
47	2164	0.149	1-(Aminoazidocarbamatoyl)-5-azido tetrazol	[34]
48	2175	0.150	5-Azido-1*H*-tetrazole	[38]
49	2208	0.151	Hydrazo-and Azo-1,3,5-triazine	[32]
50	2175	0.158	5-Azido-1-diazidocarbamatoyl tetrazol	[34]
51	2180	0.160	Carbonyl diazide, $OC(N_3)_2$	[39]
52	2230	0.195	$N_5^+Sb_2F_{11}$	[40]
53	2240	0.210	$N_5^+AsF_6^-$	[5]

respectively. In dry aprotic solvent DMSO the frequency of v_3 of the N_3^- ion of tetrabutyl ammonium azide is 2000 cm^{-1} [11]. It relates to the both free azide ion paired with tetra butyl ammonium [11] and covalent bound azide group in organic acids [12]. The v_3 mode in symmetric azide ions (N—N—N) in crystal, where the lengths of both N—N bonds are equal, absorbs at 2037.1 cm^{-1} [4], as e.g. KN_3 in KBr matrix. The increasing of frequency can be naturally explained with influence of a crystal lattice. It should be noted that the azide band changes to the high frequency range in the presence of water. In water (D_2O) solution its frequency in NaN_3 is 2043.5 cm^{-1} [13] – this "blue" shift possibly is a result of H-bond interaction.

The position of the v_3 mode in molecular N_3 groups is higher – in gaseous HN_3 molecule it is near 2140 cm^{-1} [14]; in the CH_3N_3 molecule it is near 2100 cm^{-1}. The molar intensity, measured in CH_3N_3 gas, is 1464(182) $atm^{-1}cm^{-2}$ [15]. This value is typical for fairly strong IR bands. This explains the v_3 frequency's relatively small sensitivity to the aggregate state and to intermolecular interactions in solvents.

The v_3 frequency is affected even more strongly by molecular structure. In molecular form, when azide group is connected with carbon or metal, the N_3 group cannot be treated as free and symmetrical. In these systems the symmetry of azide group is broken to a varying extent: one N—N bond is shorter while the other is longer. It should be noted that the deviation of the total length of azide groups in different structures is not big, i.e., in the limits of $2–3.10^{-2}$ Å, but the asymmetry can reach ca. 0.2 Å. For example, an asymmetry of 0.072 Å was found in the simplest organic azide CH_3N_3 molecule [16]. This is only one example from a vast body of experimental data which shows that the position of the v_3 band changes in the range of approximately 200 cm^{-1} in different organic and inorganic aside complexes.