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THE VIBRATIONAL GROUP FREQUENCY OF THE N-O• STRETCHING BAND OF NITROXIDE STABLE FREE RADICALS

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Abstract: The group frequency of the N-O radical stretching vibration has received scant attention in the literature. The few existing treatments of the vibrational spectroscopy of nitroxides are incomplete at best and potentially misleading to workers in the field. To close this gap in the available knowledge, the existing literature on the vibrational spectra of nitroxide stable free radicals is critically reviewed with particular reference to the wavenumber position of the N-O• stretching vibration, $\nu(\text{N-O}\bullet)$. Poor evidentiary bases for the assignment $\nu(\text{N-O}\bullet)$ were found in many instances. *Ab initio* Density Field Theory calculations using a model chemistry of UB3LYP at the 6-311++G(d,p) level were performed to obtain a theoretical band position of $\nu(\text{N-O}\bullet)$ for comparison with the published data. Large discrepancies between the theoretical and experimental values were found for the radical 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy, which currently sets the lower limit of the accepted wavenumber range of $\nu(\text{N-O}\bullet)$, as well as for the nitronyl and iminyl nitroxides. The wavenumber position of $\nu(\text{N-O}\bullet)$ was found to occur in the range 1450 - 1420 cm^{-1} for 5-membered cyclic nitroxides and 1395 - 1340 cm^{-1} for 6-membered cyclic and acyclic nitroxides. In nitronyl nitroxides, the symmetric

stretching vibration occurs in the region 1470 cm^{-1} , but coupling to other modes makes specific band assignments problematic for the nitronyl nitroxide group.

Keywords: nitroxide radicals, infrared spectra, Raman spectra, density field theory, aminoxyl radicals, nitroxyl radicals.

1. Introduction

The unique magnetic and chemical characteristics of stable nitroxide free radical compounds are being increasingly exploited in many areas of materials and biomedical research. Radical trapping in polymers and as EPR spin probes of oxidative states in complex systems are but two examples. Despite much research into their characterisation using magnetic techniques such as EPR and NMR, relatively little is known about the vibrational spectra of nitroxides. Because the group frequency of the N-O[•] stretching vibration, $\nu(\text{N-O}^{\bullet})$, is not listed in any of the major vibrational spectroscopy handbooks [1,2,3], the received knowledge of the band for workers in the nitroxide field stems from review articles, which variously state that $\nu(\text{N-O}^{\bullet})$ lies near 1350cm^{-1} ($1380 - 1310\text{ cm}^{-1}$) [4], or between $1380 - 1340\text{ cm}^{-1}$ [5], or $1370 - 1340\text{cm}^{-1}$ [6] or $1380 - 1339\text{ cm}^{-1}$ [7].

The first review, published in 1968 [4 - Forrester], cited the band positions for several compounds including: di(*t*-butyl)nitroxide (DTBN), from a report on its synthesis in 1961 [8], which stated that an IR band at 1345 cm^{-1} was "probably due to $\nu(\text{N-O}^{\bullet})$ "; dianisyl nitroxide from the work of [9] Otting and Kainer, who assigned a band at 1346 cm^{-1} by comparing the spectrum of the radical with that of its amine precursor; diphenyl nitroxide, from an ESR study of Pannell [10], who reported a weak IR band at 1342 cm^{-1} and tentatively assigned it to $\nu(\text{N-O}^{\bullet})$ by analogy to dianisyl nitroxide; and (*t*-butyl)-*p*-(*t*-butyl)phenyl nitroxide at 1355 cm^{-1} from the reviewers own unpublished work. In 1970, in a review of the synthesis of nitroxides, Rozantsev and Sholle [5] placed $\nu(\text{N-O}^{\bullet})$ between 1370 and 1340 cm^{-1} , additionally including nitronyl nitroxides on the basis of the work of Osieki *et al.* [11], who nominated a band at 1371 cm^{-1} as a "probable" N-O stretching peak for phenyl nitronyl nitroxide and 5-membered cyclic nitroxides based on the work of Dupeyre *et al.* [12], who simply noted, without comment, a band at 1370 cm^{-1} in the IR spectra of some 5-membered cyclic nitroxides. It should be highlighted that at the time of this review none of these assignments, with the possible exception of dianisyl nitroxide [9] had been verified.

By 1998 when Aurich published his review on the chemistry of nitroxides [4], the situation was much clearer. Aurich placed the characteristic IR absorptions for the N-O[•]

bond in the range 1380 – 1340 cm^{-1} by reference to the acyclic compounds DTBN [8], diphenylnitroxide [10] and the 6-membered cyclic nitroxides, TEMPONE VII and TEMPOL VIII [13]. By then it was clear that that assignment of $\nu(\text{N-O}^\bullet)$ was confounded by its relative weakness and the presence of geminal methyl deformations and other vibrations interfering in the region of interest. While spectral comparisons with amine or hydroxylamine precursors were successful in the case of dianisyl nitroxide, they were ambiguous at best when *t*-butyl groups were present, as is the case for many nitroxides given the protection they provide the radical moiety. In those instances, spectral comparisons with ^{15}N or ^{18}O analogues were required for confirmation. Thus, the positions of $\nu(\text{N-O}^\bullet)$ of the 6-membered rings, TEMPONE and TEMPOL, were determined to be 1380 and 1371 cm^{-1} , respectively, by ^{15}N substitution [13], and 1339 cm^{-1} in the case of TEMPO by ^{18}O substitution [14], to give a range of 1380 – 1339 cm^{-1} for 6-membered cyclic nitroxides. Finally, many years after it was first proposed, ^{15}N measurements were undertaken to confirm 1337 cm^{-1} for $\nu(\text{N-O}^\bullet)$ of the acyclic DTBN [15].

Although the basis for the proclaimed range of $\nu(\text{N-O}^\bullet)$ in the Aurich review was more rigorous than in the earlier reviews, there was nevertheless a significant oversight, of a paper published in Russian by Grigor'ev [16] in 1979, which undermined the universality of the review. In the Grigor'ev paper a ^{15}N labelling experiment is described which shows that the $\nu(\text{N-O}^\bullet)$ of imidazoline cyclic nitroxides occurs in the region around 1438 cm^{-1} . Noting that the $\nu(\text{N-O}^\bullet)$ is much stronger in the Raman spectrum than the IR, the authors measured the Raman spectrum of a number of imidazolidine and pyrroline cyclic nitroxides and assigned $\nu(\text{N-O}^\bullet)$ by analogy. They drew the following conclusions: that Raman was better suited to the study of nitroxides because $\nu(\text{N-O}^\bullet)$ is more active in the Raman than in the IR and potentially interfering geminal methyl groups bands are correspondingly less intense; and, significantly, that the $\nu(\text{N-O}^\bullet)$ of 5-membered cyclic nitroxides occurred in the range 1440 - 1420 cm^{-1} , whereas 6-membered cyclic nitroxides occurred from 1380 - 1385 cm^{-1} . It was further suggested that the position of $\nu(\text{N-O}^\bullet)$ was a function of ring size analogous to the C=O stretch of cyclic ketones. The findings

that the peak positions of 5-membered cyclic nitroxides were up to 60 cm^{-1} higher than the known nitroxide range were at odds with the reports cited in the reviews [4,5] but this fact failed to gain any traction in the relevant English language literature.

With current nitroxide researchers relying on what amounts to at times as little more than unsubstantiated conjecture, it is not surprising that errors in N-O• band assignments continue to appear in the literature. Clearly, an authoritative review of the true range of $\nu(\text{N-O}^\bullet)$ is long overdue. In a previous paper, we showed, with the aid of isotopic substitution, that DFT calculations closely modelled the band position of $\nu(\text{N-O}^\bullet)$ in the 5-membered nitroxide, 1,1,3,3-tetramethylisoindolin-2-ylloxyl (TMIO) [17]. The aim of this current research was to extend those calculations; to re-examine all published data of the nitroxide band position and compare them with the DFT calculated position with a view to identifying any anomalous assignments and to establish the true wavenumber range of the nitroxide stretching vibration. The results of this endeavour are presented here.

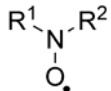
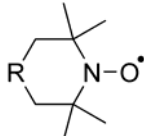
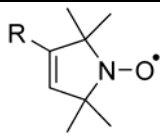
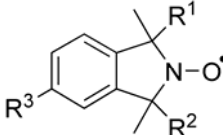
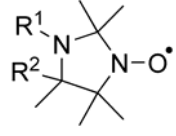
2. Experimental

Computational Methods

Calculations were performed using the Gaussian 03 [18] program and the GaussView 3.0 (Gaussian, Inc., Wallingford, CT) front end, running on an SGI Origin 3000 supercomputer comprising 116 processors and 60 GB of memory. The vibrational frequencies of the various nitroxide radicals were calculated using Density Field Theory (DFT) with UB3-LYP method and a 6-311G+(d) basis set, which has been shown to be of a sufficient level for this purpose [17]. Atomic coordinates from the crystal structure [19], where available were used as a starting point for the geometry optimisation. The calculated wavenumbers were scaled by a factor of 0.976 to correct for excess electron correlation energy. Bands were assigned by visual inspection of the vibrations using the animation feature of the GaussView 3.0 program.

3. Results and Discussion

Table 1. The structures, experimental and the DFT calculated values of $\nu(\text{N-O}^\bullet)$ and the DFT calculated CNC bond angles, and dihedral angles of the $-\text{C}(\text{NO}^\bullet)\text{C}-$ moiety are shown for a series of nitroxide radicals.

			Exp $\nu(\text{NO}^\bullet)$ cm^{-1}	DFT $\nu(\text{NO}^\bullet)$ cm^{-1}	CNC Angle $^\circ$	Planarity $\text{C}(\text{NO}^\bullet)\text{C}$ $^\circ$
Dialkyl/aryl acyclic nitroxides						
	I	R ^{1,2} : anisyl	1344 ^[9]	1325	123	180
	II	R ^{1,2} : phenyl	1342 ^[10]	1323	123	180
	III	R ¹ : phenyl, R ² : <i>t</i> -butyl	1370 ^[20]	1338	124	156
	IV	R ^{1,2} : <i>t</i> -butyl (DTBN)	1342 ^[15]	1338	128	162
	V	R ^{1,2} : CF ₃	1397 ^[21]	1360	122	172
Cyclic nitroxides 6-membered						
 Piperidine ring	VI	R: CH ₂ (TEMPO)	1339 ^[14]	1344	124	159
	VII	R: C=O (TEMPONE)	1380 ^[13]	1372	125	159
	VIII	R: CHOH (TEMPOL)	1371 ^[13]	1343	124	159
	IX	R: C=NOH	1362 ^[16]	1346	125	156
	X	R: CHOC=OPh	1350 ^[16]	1351	125	159
Cyclic nitroxides 5-membered						
 Pyrroline ring	XI	R: CONH ₂	1310 ^[22] 1438 ^[16]	1423	114	171
	XII	R: COOCH ₃	1435 ^[16]	1410	115	180
 Isoindoline ring	XIII	R ^{1,2} : Ph	1366 ^[23]	1430	115	166
	XIV	R ^{1,2} : CH ₃ , R ³ : COOH	1392, 1367 ^[24]	1436	116	180
	XV	R ^{1,2} : CH ₃ (TMIO)	1428 ^[17]	1438	115	180
 Imidazolidine ring	XVI	R ¹ : Me, R ² : C≡N	1438±5 ^[16]	1407	114	163
	XVII	R ^{1,2} : H		1410	114	170
	XVIII	R ¹ : OMe, R ² : Me		1419	113	160

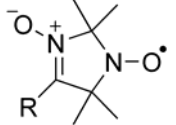
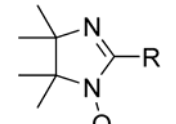
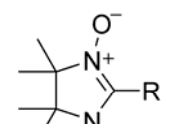
 Imidazoline ring	XXI	R: Me	1436 ^[16]	1407	114	180
	XXII	R: CH ₂ Br	1436 ^[16]	1410	114	174
 Iminyls	XXIII	R: pyrazol-4-yl (PzIN)	1370 ^[25]	1404	109	168
	XXIV	R: phenyl		1402	109	171
 Nitronyls	XXV	R: p-nitrophenyl (NPNN)	2457, 2695 ^[26]	1427, 1417	108	173
	XXVI	R: pyrazol-4-yl (PzNN)	1367 ^[25]	1423, 1410	112	170
	XXVII	R: phenyl	1371 ^[11]	1436, 1386	112	171

Table 1 shows the structures, the experimental DFT calculated peak positions of $\nu(\text{N-O}^\bullet)$, the calculated angle of the CNC bond and the calculated dihedral angle of the $-\text{C}(\text{NO}^\bullet)\text{C}$ -moiety of a series of nitroxide radicals for which published wavenumber positions of $\nu(\text{N-O}^\bullet)$ are available. Good agreement between the experimental and theoretical values was obtained in most instances but significant differences were found for radicals **XI**, **XIII**, **XIV**, **XXIII**, **XXIV** and **XXV**.

The radical **XI**, 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy, is an interesting case in point. The spectrum was first reported in a study [22] by Brière *et al.* in which the IR spectra of various 5-membered cyclic nitroxides were compared with those of the corresponding hydroxylamine analogues. The authors concluded that an unequivocal assignment of $\nu(\text{N-O}^\bullet)$ could not be deduced from the spectra and so, although an additional band was observed at 1310 cm^{-1} in the spectrum of the radical, it was not assigned. These conclusions were apparently misconstrued in the Aurich review [4], in which 1310 cm^{-1} was given as the established position of $\nu(\text{N-O}^\bullet)$ of radical **XI**. This misinterpretation assumed undue significance, as 1310 cm^{-1} is the current lower limit of the "accepted" wavenumber range of $\nu(\text{N-O}^\bullet)$. Radical **XI** was one of two pyrroline

nitroxides examined in the Raman study of Grigor'ev [16], discussed above. In that study, a band of medium intensity at 1438 cm^{-1} in the Raman spectrum of **XI** was assigned to $\nu(\text{N-O}^\bullet)$ by analogy to the imidazolidine cyclic nitroxides. The DFT calculated position, 1423 cm^{-1} , accords with this much higher wavenumber position. As the evidence supporting the 1310 cm^{-1} assignment is weak or even non-existent, it can be disregarded as a candidate for the lowest wavenumber limit which now defaults to 1340 cm^{-1} for TEMPO.

The synthesis of isoindoline ring nitroxides is an active area of research and here too erroneous assignments have been made in the infrared characterisation of these compounds. For instance, the published value for $\nu(\text{N-O}^\bullet)$ of 1,3-dimethyl-1,3-diphenyl-isoindolin-2-yloxy (**XIII**), is 1366 cm^{-1} [23]. This band was most likely assigned by reference to the reviews available at that time (1998) but DFT calculations suggest that $\nu(\text{N-O}^\bullet)$ of **XIII** should be nearer to 1436 cm^{-1} than 1366 cm^{-1} . Band assignments for $\nu(\text{N-O}^\bullet)$ in the region of $1390\text{ -}1330\text{ cm}^{-1}$ have also been published for various 5 and 5,6-substituted TMIO nitroxides, [24,27]; for example see 5-carboxy-1,1,3,3-tetramethylisoindolin-2-yloxy or 5-carboxyTMIO (**XIV**) in Table 1, first described by the latter two authors of this present paper. In this instance it is known that $\nu(\text{N-O}^\bullet)$ was assigned by reference to the aforementioned reviews [5,6]. Since then, we undertook isotopic substitution studies and *ab initio* calculations which established conclusively that $\nu(\text{N-O}^\bullet)$ of the unsubstituted isoindoline nitroxide, TMIO (**XV**) occurs at 1428 cm^{-1} [17]. Substitutions on the phenyl ring of the isoindoline moiety are unlikely to substantially affect the band position of $\nu(\text{N-O}^\bullet)$ and indeed DFT calculations confirm that this is the case. For **XIV** the theoretical value of $\nu(\text{N-O}^\bullet)$ is 1436 cm^{-1} , which corresponds to a peak at 1427 cm^{-1} in the IR spectrum of that compound. These examples of mistakes in our own laboratory and others emphasise the need for a proper analysis of the IR spectrum of nitroxides.

In 2001 Catala, *et al.*, in an article on the synthesis and characterisation of pyrazol-4-yl substituted α -nitronyl and α -iminyl nitroxide radicals, attributed IR bands at 1370 and 1367 cm^{-1} for PzIN (**XXI**) and PzNN (**XXIV**), respectively, to $\nu(\text{N-O}^\bullet)$ on the basis that

this is the "normal position for this band" [25]. The nitronyl radicals, having two NO moieties in a 5-membered ring, are a special case and will be discussed later. However for the α -iminyl nitroxide, it would appear that acceptance of the "received wisdom" by Catala, *et al.* may have led to an incorrect conclusion. The α -iminyl nitroxide is a 5-membered cyclic nitroxide and so, according to Grigor'ev [16], should occur in the region 1440 - 1420 cm^{-1} . The DFT calculated position of 1421 cm^{-1} falls within this range casting grave doubt on the 1370 cm^{-1} assignment.

Nitronyl nitroxides (**XXIII** - **XXV**) have two N-O groups in a 5-membered imidazolidine ring where the single radical electron is shared in a delocalised orbital across the O-N-C-N-O atoms. A reasonable expectation is that the vibrations of the NO groups would couple to give an in-phase and an out-of-phase mode. The Raman spectrum of p-NPNN (**XXIII**), has been reported by Mo *et al.* [26], who assigned two weak bands at 2457 and 2695 cm^{-1} to $\nu(\text{N-O}^{\bullet})$. This seems unlikely as knowledge of the bonding of N-O in this molecule dictates that it falls somewhere between N=O and N-O, i.e. between 1600 and 1000 cm^{-1} . Inspection of this region of the published Raman spectrum [26] reveals two dominant bands at 1600 and 1350 cm^{-1} due to ring quadrant stretch and the NO_2 stretch, respectively, of the para-nitrophenyl moiety and, between these strong peaks, three bands of medium intensity at 1525, 1469, 1419 and a shoulder at 1382 cm^{-1} . A comparable pattern of peaks is obtained by DFT calculations of the Raman spectrum of p-NPNN. By comparing bands between the experimental and theoretical spectra and examining of the calculated motion for each particular mode it can be shown that the band at 1469 cm^{-1} has contributions from two modes both of which involve the coupled in-phase NO stretching with geminal methyl deformation modes. The out-of-phase N-O vibration is predicted to occur at 1474 cm^{-1} but has very low Raman activity and only weak strength in the IR. There is considerable coupling between N-O and the various phenyl ring modes, C-N stretch and CH_3 deformations that occur between 1450 and 1330 cm^{-1} .

Factors affecting $\nu(\text{N-O}^{\bullet})$

As noted above, Grigor'ev, et al. [16] suggested that the wavenumber of the nitroxide stretch was a function of ring size in an analogous manner to the carbonyl band of cyclic ketones and that the $\nu(\text{N-O}^\bullet)$ for 5-membered cyclic nitroxides is 40 – 60 cm^{-1} higher than 6-membered rings. The DFT calculations and further experimental work [17] in fact confirm that for a wide range of nitroxides with a ring size of 5, encompassing, pyrroline, imidalolidine, imidazoline, iminyl and isoindoline, $\nu(\text{N-O}^\bullet)$ occurs in a range 1435 – 1400 cm^{-1} . The size of the ring places a constraint on the CNC bond angle. For 5-membered rings the CNC angle ranges from 109 to 116°, while for 6-membered rings, ranges from 123 to 125°. The acyclic nitroxides have similar CNC angles (121 – 127°) to the 6-membered cyclic nitroxides and $\nu(\text{N-O}^\bullet)$ occurs in approximately the same range (1360 – 1338 cm^{-1}). It seems reasonable to expect that the formation of the N-O π -bond would be favoured by a planar geometry of the C(NO)C moiety and so planarity could be another factor affecting the band position of $\nu(\text{N-O}^\bullet)$. However, inspection of the calculated dihedral angles listed in Table I, suggests that it is not a major influence. This point is perhaps best illustrated by comparing DTBN, where the N-O $^\bullet$ is tilted at 17° to the plane of the CNC, to diphenylnitroxide and TMIO, both of which are planar. The N-O $^\bullet$ stretch of DTBN is much nearer to diphenylnitroxide (1338 cf. 1342 cm^{-1}) than to the 5-cyclic TMIO (1428 cm^{-1}).

4. Conclusions

Comparisons of the experimentally determined band positions of $\nu(\text{N-O}^\bullet)$ with DFT calculated band positions for a wide range of nitroxides uncovered several band assignment errors in the literature. The accepted range of $\nu(\text{N-O}^\bullet)$ has been shown to be incorrect in the low wavenumber limit due to erroneous assignments and, in the English language literature at least, incorrect in the high wavenumber region because significant work on the Raman spectra of 5-membered cyclic nitroxides was overlooked. In the discussion above it has been established here that the group frequency of the nitroxide N-O $^\bullet$ stretching vibration, $\nu(\text{N-O}^\bullet)$ occurs in the range 1450 - 1340 cm^{-1} . For acyclic and 6-membered cyclic nitroxide $\nu(\text{N-O}^\bullet)$ occurs from 1400- 1340 cm^{-1} . For 5-membered

cyclic nitroxides, $\nu(\text{N-O}^\bullet)$ occurs in the range 1435 - 1400 cm^{-1} . In nitronyl nitroxides, the symmetric stretching vibration occurs are expected to occur near 1470 cm^{-1} , but specific band assignments are problematic due to the strong coupling between the N-O^\bullet bond vibrations and those of the phenyl ring, the C-N and methyl groups.

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