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DFT Calculations of the Molecular Force Field of Vanadyl Nitrate, $VO(NO_3)_3$

S. A. Brandán,[a] C. Socolsky,[a] and Aida Ben Altabef*[‡][a]

Keywords: Vanadium; Coordination modes; Density functional calculations; Ab initio calculations; Vibrational spectroscopy

Abstract. A structural and vibrational theoretical study for vanadyl nitrate was carried out. The Density Functional Theory (DFT) has been used to study vibrational properties. The geometries were fully optimised at the B3LYP/6-31G*, B3LYP/6-311G* and B3LYP/6-311+G* levels of theory and the harmonic vibrational frequencies were evaluated at the same level. The calculated harmonic vibrational frequencies for vanadyl nitrate are consistent with their experimental IR and Raman spectra in gas and liquid phases. Through these calculations we obtained a precise knowledge of the normal modes of vibration considering the coordination mode adopted by the nitrate group in the mirror plane as monodentate and bidentate. A total assignment of the observed bands in the vibrational spectra for vanadyl nitrate is proposed in this work. The nature of the V−O and V←O bonds in the compound was systematically and quantitatively investigated by means of the Natural Bond Order (NBO) analysis. The topological properties of the electronic charge density were analysed employing Bader's Atoms in Molecules theory (AIM).

1. Introduction

The structure of isolated vanadyl nitrate $VO(NO_3)_3$ has been determined in the gas phase by electron diffraction (GED) and molecular orbital calculations [1]. This compound presents vibrational properties, which were imperfectly characterized and only the main features of the infrared spectrum in liquid and gas phases were published previously. We have assigned some bands observed in the vibrational spectra of vanadyl nitrate [2]. This compound has nitrate ligands that can act as monodentate and bidentate ligands comparable to $CrO_2(NO_3)_2$ [3, 4]. Hence, it is in our interest to study this liquid compound because the coordination mode adopted by the nitrate groups and the stereochemistry of this compound are important in relation to its vibrational properties and its chemical reactivity [5−7]. This pale yellow viscous liquid can be obtained with the reported method by *Harris* et al. [8]. The aim of this work was to carry out a theoretical study of this compound with the methods of quantum chemistry and to use available experimental data reported in literature [1, 2] to get a better understanding of the vibrational properties of vanadyl nitrate. We expected that a detailed knowledge of the normal vibration modes and the coordination mode of the nitrate groups would allow a complete vibrational assignment of the spectra of this molecule. For this purpose, the normal mode calculations were accomplished by a generalized valence force field (GVFF). In this work, we performed calculations of the geometry and frequencies by using DFT methods. The vibrational analysis was carried out considering the three nitrate groups of vanadyl nitrate to be formed at first by one monodentate group, then by two bidentate groups and finally by three bidentate ligands. At present there are no published experimental or high level theoretical studies on the force field of vanadyl nitrate. Hence, obtaining reliable parameters by theoretical methods is an appealing alternative. These parameters may be used to gain chemical and vibrational insights into related compounds. The selection of the adequate method and basis sets is very important to evaluate not only the best level of theory but also the best basis set to be used to reproduce the experimental geometry and frequencies.

Smart et al. [1] predicted the final structure of vanadyl nitrate with the B3LYP method. Moreover, in different compounds containing transition metals, such as V and Cr [3, 9−12], the HF and MP2 methodologies are much less satisfactory than the DFT techniques. In $VO_2X_2^-$ (X = F, Cl) [9], $[VOCl_4]^-$ anions [11] and the compound $[AsPh_4][CrOCl_4]$ [12] the inclusion of polarization functions in the basis set is important to recieve a better agreement with the according experimental structures. On the other hand, in the VOX_3 (X = F, Cl, Br, I) series the optimized structure that reproduces the experimental parameters better was obtained in the B3PW91/6-311G calculation. In all above cases, the B3PW91 or B3LYP methods produced the best results for the frequencies [13]. *Bell* et al. [14] found in

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a recent study of the structures and vibrational spectra of chromium oxo anions and oxyhalides that the B3LYP/Lanl2DZ combination gives the best fit for the structures and observed vibrational spectra of these compounds. In this case, we used DFT calculations to study the structure and the vibrational properties of $VO(NO_3)_3$. The normal mode calculations were accomplished by a GVFF. Herein we demonstrate that a DFT molecular force field for the vanadyl nitrate, computed by using 6-31G* and 6-311G* basis sets is well represented. We obtained the force field scaling factors, which produce a satisfactory agreement between the calculated and experimental vibrational frequencies of vanadyl nitrate. The normal mode assignments, in terms of the potential energy distribution (PED), are in agreement with those obtained from the normal coordinate analysis. Also, the nature of the two types of V−O and V←O bonds in the vanadyl nitrate compound was systematically and quantitatively investigated by the Natural Bond Order (NBO) analysis [15−17]. In addition, the topological properties of electronic charge density are analyzed by employing *Bader's* atoms in molecules theory (AIM) [18].

2. Experimental Section

The infrared spectra in liquid and gas phases and the Raman spectra of liquid vanadyl nitrate, $VO(NO_3)_3$, were taken from a previous study [2] where the compound was obtained as reported in reference [8]. Figure 1, Figure 2 and Figure 3 show the infrared spectra in the liquid and gas phases whereas Figure 4 shows the Raman spectra of the liquid compound.

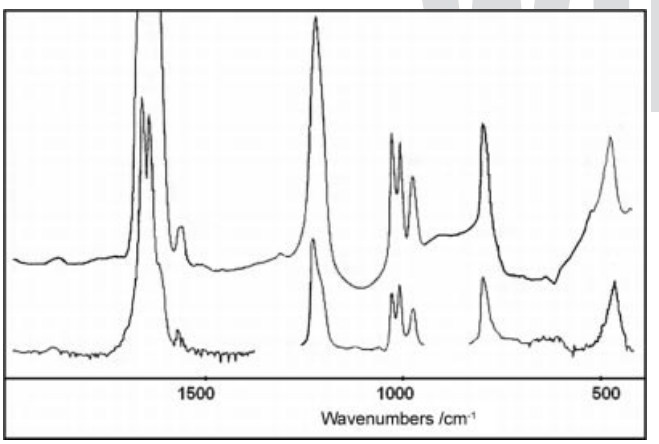

Figure 1. The infrared spectra of gaseous (lower, left absorbance scale) and liquid (upper, right absorbance scale) $VO(NO_3)_3$. The discontinuities in the gas spectrum trace correspond to regions of HNO_3 absorption.

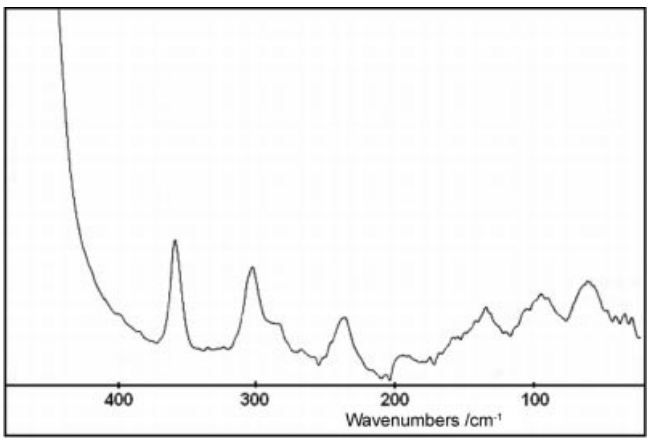

Figure 2. The infrared spectrum of liquid $VO(NO_3)_3$ in the low wavenumbers region.

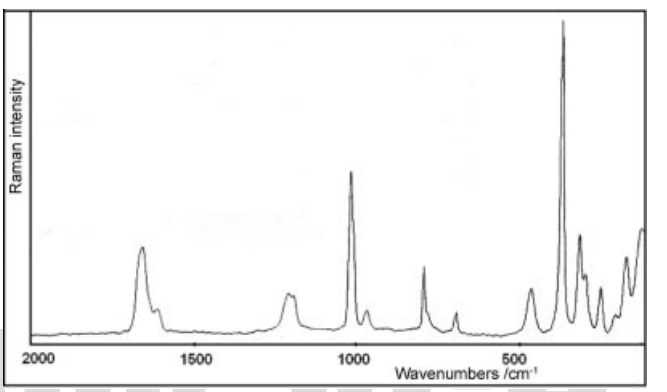

Figure 3. The Raman spectrum of liquid $VO(NO_3)_3$.

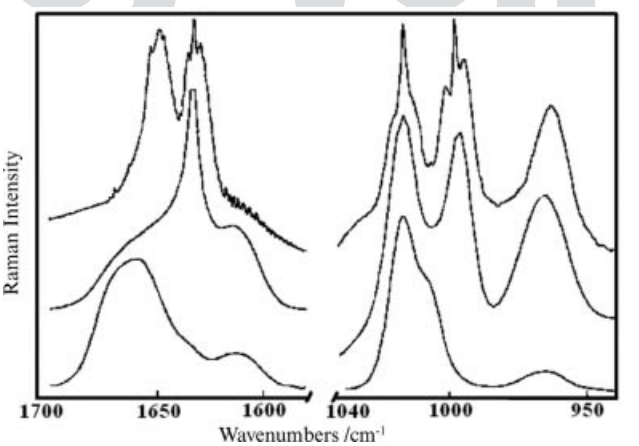

Figure 4. Expanded regions of the spectra of $VO(NO_3)_3$. Upper, infrared spectrum of the gas; middle, infrared spectrum of the liquid; lower, Raman spectrum of the liquid.

3. Computational Details

All calculations were made by using the Gaussian 03 [19] set of programs run on a Pentium IV PC working under the Windows operative system. Structure calculations were performed by using standard gradient techniques and the default convergence criteria as implemented in GAUSSIAN. The starting point for the structure optimization was modelled with the *GAUSSIAN View* program [20]. The calculations were made with hybrid DFT methods. In this technique, *Becke*π*s* three parameter functional and the non-local correlation provided by *Lee-Yang-Parr's* (B3LYP)

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[21, 22] expressions were used, as implemented in the GAUSSIAN program. The STO-3G, 3-21G*, 6-31G, 6-31G*, 6-31+G, 6-31+G*, 6-311G, 6-311G*, 6-311+G and 6-311+G* basis sets were used. The normal mode analysis using 6-31G*, 6311G* and 6-311+G* basis sets was carried out for the compound.

The harmonic force field in cartesian coordinates for vanadyl nitrate, which resulted from the calculations was transformed to "natural" internal coordinates [23] by the MOLVIB program [24, 25]. The natural coordinates for the two types of vanadyl nitrate considered (case 1: one group nitrate as monodentate and two with bidentate coordination; case 2: three nitrate groups as bidentate coordination) are shown in Tables S1 and S2 of the supporting material and have been defined as proposed by *Fogarasi* et al. [26]. The numbering of the atoms for the two cases is described in Figure 5 and Figure 6. The force field was scaled and refined by using the MOLVIB program, in which the force constants are multiplied by scale factors until reproducing the experimental frequencies as well as possible. The PED components greater than or equal to 10 % are subsequently calculated with the resulting Scaled Quantum Mechanics (SQM) force field.

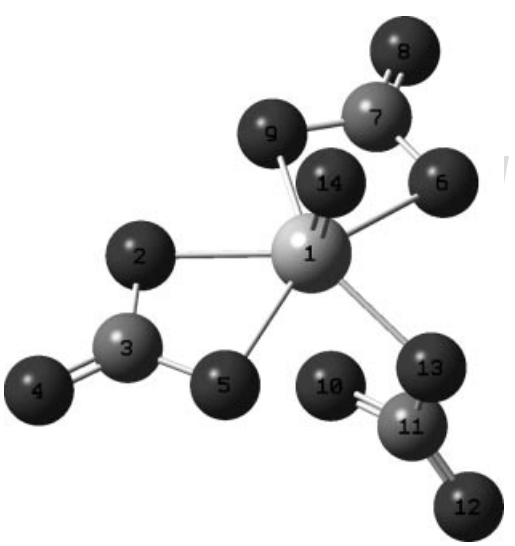

Figure 5. The molecular structure of $VO(NO_3)_3$ considering the nitrate groups as two bidentate and one monodentate ligands.

NBO analysis was then performed using 6-31G*, 6-311+G and 6-311+G* basis sets by the NBO 3.1 program [27] included in GAUSSIAN 03 package programs [18]. The topological properties of the charge density in all systems studied were computed with the AIM2000 software [28].

4. Results and Discussion

4.1. Structure Calculations

The structure of isolated vanadyl nitrate, $VO(NO_3)_3$ has been determined in the gas phase by electron diffraction (GED) and molecular orbital calculations [1]. $VO(NO_3)_3$

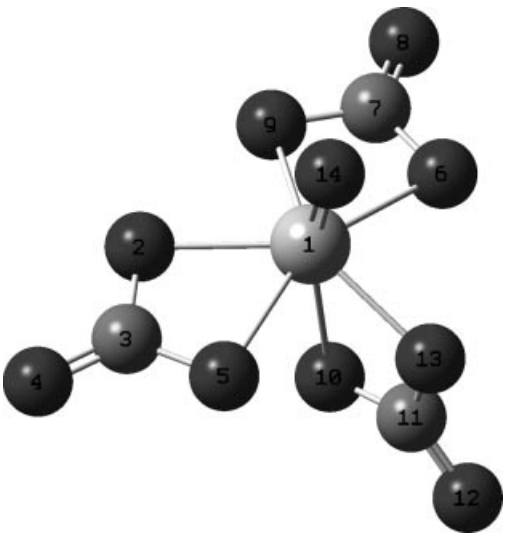

Figure 6. The molecular structure of $VO(NO_3)_3$ considering the nitrate group as three bidentate ligands.

adopts a structure that is best described as distorted pentagonal bipyramid with an overall C_s symmetry. The structure contains three bidentate planar nitrate groups asymmetrically bound to the vanadium atom. A single nitrate group lies in the mirror plane, the two other nitrate groups are on the other side of this plane and stand almost perpendicular to it.

The B3LYP structures obtained for vanadyl nitrate with the different basis sets have C_s symmetry and correspond to a true minimum similar to the experimental structure obtained by *Smart* et al. [1]. Table 1 shows the comparison of the total energies and dipole moment values for vanadyl nitrate calculated with the B3LYP method using different basis sets. The more stable structure is obtained by using the B3LYP/6-311+G* method combined with a diffuse function basis set. In this case, the method with a higher dipole moment value does not agree with the method that gives the more stable structure indicating that the dipole moment value is not related to the stability of the molecule. The results of the calculations with all basis sets used are reported in Table S3. According to these results, the methods and basis sets that reproduce the experimental bond lenghts for $VO(NO_3)_3$ best are B3LYP/6-311G* and B3LYP/6-311+G*, where the mean difference (RMSD) for bond lengths is 0.041 Å and B3LYP/6-311G* for angles with RMSD of 4.11°. If diffuse functions are included in the basis set, the mean difference value for the bond angle (with 6-311+G* basis set, 4.24°) improves slightly. The inclusion of polarization functions is important to have a better agreement in the distance values. The use of the B3LYP calculations gives a somewhat less satisfactory agreement in the structural parameters using the STO-3G basis set. All B3LYP calculations also represent the coordination around V as a distorted pentagonal bipyramid where the nitrate

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groups act as bidentate ligands and are asymmetrically bond to V.

Table 1. Total energy and dipole moment for vanadyl nitrate at B3LYP method.

Basis set	ET (Hartree)	μ (D)
STO-3G	−1838.10633505	0.83
3-21G*	−1850.67617201	0.97
6-31G	−1859.83839857	1.14
6-31G*	−1860.20723715	1.19
6-311G	−1860.17015764	1.25
6-31+G	−1859.88990863	1.29
6-31+G*	−1860.24587692	1.36
6-311G*	−1860.50424411	1.30
6-311+G	−1860.20723715	1.19
6-311+G*	−1860.54009169	1.23

The bond orders, expressed by means of the Wiberg indices matrix for vanadyl nitrate, are given in Table S4. In Table S5 they are observed together with the Mulliken atomic charges using different basis sets. In all cases, the bond order values for the V and O atoms involved in the V−O bonds increase when the basis sets size increases. It can be seen that the vanadium atom forms seven bonds, one V=O bond (bond order 2.2560 using 6-311+G* basis sets), four V−O bonds (two with bond orders of 0.4169 and two with bond orders of 0.4718 using 6-311+G* basis set), another V−O bond with bond order of 0.5581 and one V←O bond (bond order of 0.1852 with 6-311+G basis set and 0.1858 using 6-311+G* basis set). The bond order value of this last bond is slightly bigger than the values for the Cr←O bond order in $CrO(NO_3)_2$ (0.1821 using 6-311+G basis set) [3]. These observations cannot be explained by the electronegativities of the Cr (1,66) and V (1,63) atoms or by the Mulliken atomic charges but rather by the natural charges of the O, Cr and V atoms in both compounds as can be seen in Table 2. These natural atomic charges of O and Cr in the chromyl compound calculated by using a 6-311+G basis set are −0.40 and 1.16, respectively, whereas in the vanadyl compound the charges of the O and V atoms obtained by using the same basis set are −0.44 and 1.42, respectively.

In the B3LYP calculations, one O=V−O−N dihedral angle is 180° and corresponds to a unique asymmetric nitrate group, whereas the remaining two O=V−O−N dihedral angles are 90° and correspond to a nitrate group that is more symmetrically coordinated. In this last case, the two nitrate groups are almost planar with the V atom.

The intermolecular interactions for vanadyl nitrate have been analyzed with *Baderπs* topological analysis of the charge electron density, $\rho(r)$ by means of the AIM program [28]. For this study, we only considered the 6-311+G* basis set because there are numerous references where the quality of the basis set has no influence on the topological results [29, 30]. The localization of the critical points in the $\rho(r)$ and the values of the Laplacian at these points are important for the characterization of the molecular electronic structure in terms of nature and magnitude of the interaction. The detailed data of the molecular models for vanadyl nitrate showing its critical points in charge density is shown in Figure 7. The analyses of the V−O bonds critical points

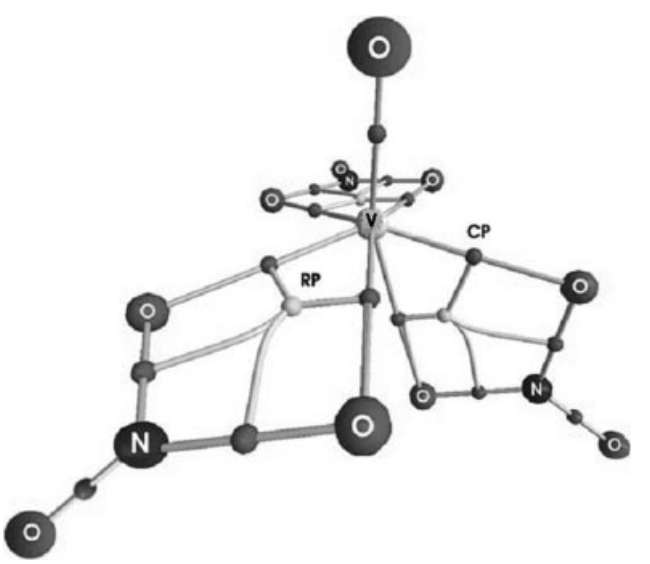

Figure 7. The critical points of the charge density for $VO(NO_3)_3$.

Table 2. Wiberg Index and Natural atomic charges (NAC) of vanadyl nitrate at different level of theory.

	6-31G*		6-311G*		6-311+G		6-311+G*	
	NAC	Wiberg Index	NAC	Wiberg Index	NAC	Wiberg Index	NAC	Wiberg Index
1. V	1.63893	4.7364	1.40464	4.9177	1.42260	5.4868	1.41563	4.9824
2. O	−0.46089	2.0917	−0.43741	2.1194	−0.40464	2.5456	−0.42700	2.1299
3. N	0.76145	4.0704	0.76858	4.0702	0.63861	2.5456	0.73140	4.0768
4. O	−0.25330	2.2263	−0.25006	2.2263	−0.19158	2.1359	−0.23529	2.2274
5. O	−0.45563	2.0907	−0.43782	2.1146	−0.40497	4.0038	−0.42306	2.1320
6. O	−0.45563	2.0907	−0.43782	2.1146	−0.40497	2.0815	−0.42306	2.1320
7. N	0.76145	4.0704	0.76858	4.0702	0.63861	2.2298	0.73140	4.0768
8. O	−0.25330	2.2263	−0.25006	2.2263	−0.19158	2.1359	−0.23529	2.2274
9. O	−0.46089	2.0917	−0.43741	2.1194	−0.40464	4.0038	−0.42700	2.1299
10. O	−0.50691	1.9760	−0.49736	1.9879	−0.43873	2.0815	−0.47029	2.0253
11. N	0.75285	4.0676	0.76180	4.0680	0.63215	2.2298	0.72381	4.0744
12. O	−0.27430	2.1978	−0.27202	2.1984	−0.21493	5.4868	−0.25908	2.1981
13. O	−0.47089	2.0916	−0.44542	2.1236	−0.41185	2.5456	−0.43694	2.1343
14. O	−0.32296	2.4651	−0.23820	2.5433	−0.26407	2.5456	−0.26523	2.5369

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in the compound studied are reported with the mentioned basis set in Table 3. Two important observations could be made; in one case only the V1←O10 bond critical point has the typical properties of the closed-shell interaction. Here, the value of ρ(r) is relatively low (0.05 and 0.3 a.u.), the relationship $|\lambda 1|/\lambda 3$ is < 1, and the Laplacian of the electron density, $\nabla^2\rho$ (r) (0.04 and 0.2 a.u.), is positive indicating that the interaction is dominated by the contraction of charge away from the interatomic surface toward each nucleus [30−36]. The other important observation is related to the topological properties of the two pairs of bond critical points (V1−O2 with V1−O9 and V1−O5 with V1−O6) because in both cases they are the same, as shown in Table 3. The interactions V1−O13 and V1=O14 are different from other bonds, which obtain characteristics of shared interactions, i.e. the value of electron density at the bond critical point is relatively high indicating that the electronic charge is concentrated in the internuclear region. Moreover, the (3+1) critical point, as shown in Figure 7, for vanadyl nitrate would confirm the three bidentate nitrate groups in the structure. The seven critical points and the three ring points of the electron density obtained by AIM analysis reveals that the coordination mode adopted by the nitrate groups in vanadyl nitrate is bidentate. Those above B3LYP level results analyzed for vanadyl nitrate agree with the structure observed by GED and strongly support the conclusions reported previously about the nature of the coordination of the V atom for this compound [1].

Table 3. Analysis of V−O bond critical points in vanadyl nitrate (The quantities are in atomics units).

	B3LYP/6-311+G*						
Bond	V1−O2	V1−O5	V1−O6	V1−O9	V1←O10	V1−O13	V1=O14
ρ (r)	0.0877	0.0769	0.0769	0.0877	0.0463	0.1043	0.3156
$\nabla^2\rho$ (r)	0.3134	0.2833	0.2833	0.3134	0.1982	0.3514	1.0328
λ1	−0.1557	−0.1269	−0.1269	−0.1557	−0.0577	−0.1950	−0.6569
λ2	−0.1423	−0.1190	−0.1190	−0.1423	−0.0540	−0.1827	−0.6561
λ3	0.6114	0.5293	0.5293	0.6114	0.3099	0.7291	2.3459
$\|\lambda 1\|/\lambda 3$	0.2546	0.2397	0.2397	0.2546	0.1862	0.2674	0.2800

Table 4. Observed and calculated frequencies (cm^{-1}) for vanadyl nitrate.

[a]IR, Gas	[a]IR, Liquid	[a]Raman, Liquid	SQM#, B3LYP/6-31G*	[a]Assignment	[b]Assignment (Two nitrate bidentate)	[b]Assignment (Three nitrate bidentate)
1888	1880 vvw			1198 + 688 = 1886		
1648	1655 sh	1659 (31) p	1650	νN=O ip (A′)	νN=O ip	νN=O ip
1635						
1632	1633 (100)	1633 sh	1634	νN=O op (A″)	νN=O op	νN=O op
1629						632 + 997 = 1629
1612 sh	1612 (41)	1612 (12) dp	1616	νN=O ip (A′)	ν_a NO_2 *	νN=O*
1564	1560			2 x 783 = 1566		
	1306			1006 + 303 = 1309		
1216.3			1225	ν_a NO_2	ν_s NO_2 *	ν_a NO_2 *
1211 sh	1205 (31)	1209 (16) dp	1217	ν_a NO_2 antisymm. ip (A′)	ν_a NO_2 ip	ν_a NO_2 ip
1198 br		1196 (15) dp	1203	ν_a NO_2 antisymm. op (A″)	ν_a NO_2 op	ν_a NO_2 op
1020 sh						1635−632 = 1023
1016.3	1016 (18)	1017 (52) p	1016	νV=O	νV=O	νV=O
1012 sh						
1006.2		1006 sh p?	999	ν_s NO_2 ip	ν_s NO_2 ip	ν_s NO_2 ip
1000.5						
997.5	996 (16)		990	ν_s NO_2 op	ν_s NO_2 op	ν_s NO_2 op
994.4			990	γN=O op, γN=O ip		γN=O op, γN=O ip
962.5	965 (13)	966 (12) dp	955	ν_s NO_2	νN-O*	ν_s NO_2*
	895		862	2 x 454 = 908	γN=O*, γN=O ip	γN=O*, γN=O ip
786			851		γN=O op	γN=O op
783	783 (18)	789 (26) p	786	δNO_2 ip	δNO_2 ip	δNO_2 ip
775 br		775 sh dp?	766	δNO_2 op	δO=N−O*, δNO_2 op	δO=N−O*, δNO_2 op
	690 ?	688 (13) p	679	δO=N−O	δO=N−O ip, δNO_2	δO=N−O ip, δO=N−O*
	632		664	358 + 283 = 641	δO=N−O op	δO=N−O op
	457 (17)	454 (17) dp	462	νV−O	νV−O*, ν V−O	νV−O
	357 (0.7)	358 (100) p	361	νV−O	νs V−O	νs V−O*
	301 (0.4)	303 (34) p	297	νV−O	νV−O	νV−O
	283	285 dp	289		δVO_2, ρVO_2	δVO_2, ρVO_2
	234	238 (18) dp	237		δVO_2, δV−O−N	δVO_2, νa V−O*
	193	192 dp	177		τNO_2*	τNO_2*
		158 (32) dp	154		δVO_2	δVO_2
	133		144		τNO_2 op	τNO_2 op
		110	104		δVO_2, τwN=O*	δVO_2, τwN=O*
	93		76		τNO_2 ip	τNO_2 ip
	59		62		δVO_2	δVO_2

Abbreviations: ν = stretching, δ = deformation, ρ = rocking, wag (γ) = wagging, τw = torsion, a = antisymmetric, s = symmetric, op = out of phase, ip = in phase. [a] Ref [2]; [b] This work; * A single nitrate group lies in the mirror plane; # Three nitrate bidentate.

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4.2. Vibrational Analysis

The structure of vanadyl nitrate has C_s symmetry and 36 vibrational normal modes, all vibrations are IR and Raman active including 21 A′ (planar) + 15 A″ (out-of-plane). The infrared spectra of the compound in liquid and gas phases and the Raman spectra of the liquid sample are visualized in Figures 1−4. The frequencies corresponding to the observed bands are collected in Table 4, the proposed assignment is also included. The spectra are quite similar to those of $CrO_2(NO_3)_2$ [37], but as depicted in Figure 4, the spectrum of gaseous $VO(NO_3)_3$ shows bands with a rotational structure, a feature that was not observed for the chromium compound.

The molecular structure of vanadyl nitrate initially proposed by *Addison* et al. [38] with two equivalent bidentate nitrate groups approximately normal to the V=O bond and to the third nitrate group. The third nitrate group can be either a monodentate or a bidentate ligand, as shown in the solid complex of vanadyl nitrate with acetonitrile [39]. As it is impossible to make a clear distinction between monodentate and bidentate nitrate groups based on infrared and Raman spectra alone [4, 38], we performed this study taking into account two cases as mentioned above. In one case, a single nitrate group lies in the mirror plane as a monodentate and two nitrate groups with bidentate coordination are in the perpendicular plane. In the second case the three nitrate groups have bidentate coordination. In both cases, the treatments of the vibrational modes of the bidentate coordinated nitrate were made as a ring of four members.

The observed and calculated frequencies for vanadyl nitrate considering the two possibilities are given in Table 4.

Table S6 shows the calculated harmonic frequencies for vanadyl nitrate using the B3LYP method with different basis sets. In all cases, the theoretical values were compared with the respective experimental values by means of the RMSD values. It can be seen that the best results are obtained with a B3LYP/6-311+G* calculation and that the introduction of polarization and diffuse functions is essential to have a good approximation to the experimental values. We will refer to the results obtained at B3LYP level with 6-31G*, 6-311G* and 6-311+G* basis sets (Tables S6-S12).

Vibrational assignments were made on the basis of the PED in terms of symmetry coordinates and by comparison with molecules that contain similar groups [2−8, 10, 37−48]. The calculated infrared spectra for vanadyl nitrate using the 6-31G*, 6-311G* and 6-311+G* basis sets approximations can bee seen in Figure 8, whereas the corresponding calculated Raman spectra are given in Figure 9. The theoretical Raman spectrum of vanadyl nitrate has a good agreement with the experimental spectrum especially in the lower frequencies (1400−50 cm^{-1}) (Figure 10).

The assignment of the most important groups for the compound studied with the two proposed cases is discussed next.

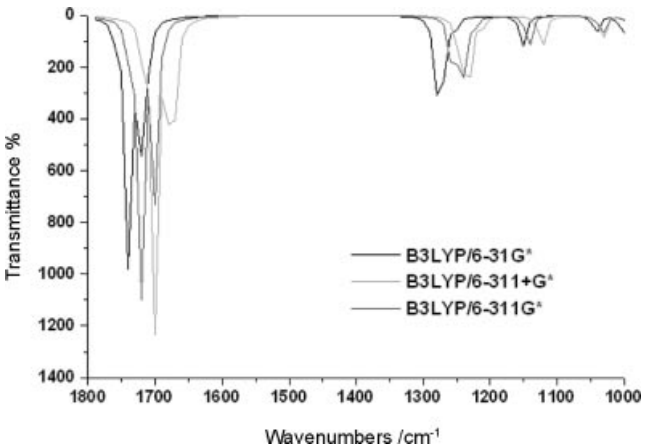

Figure 8. Theoretical Infrared spectrum of $VO(NO_3)_3$ at different levels of theory.

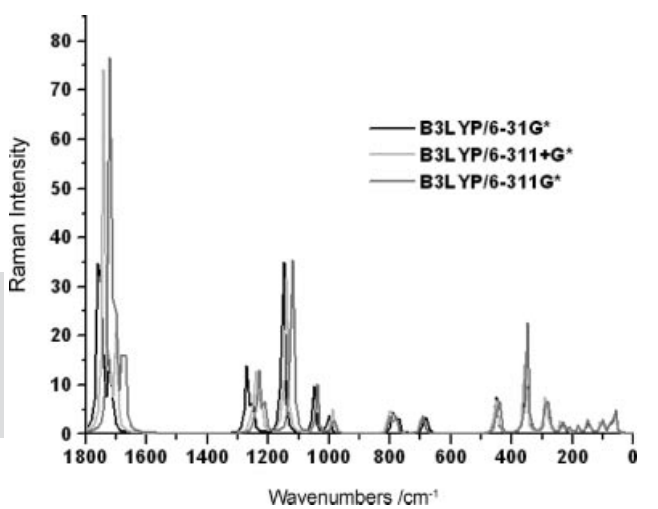

Figure 9. Theoretical Raman spectrum of $VO(NO_3)_3$ at different levels of theory.

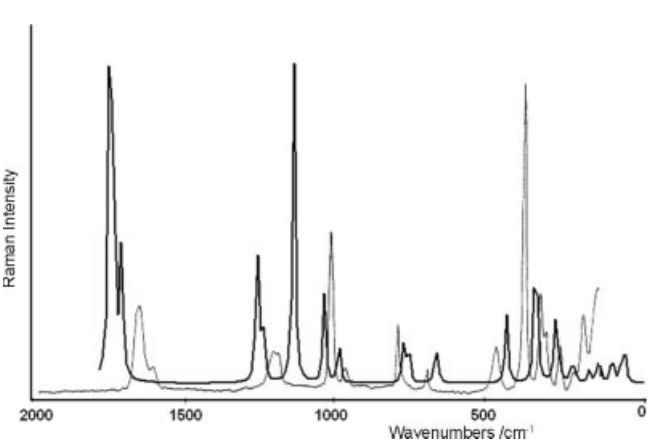

Figure 10. Experimental (bottom) and theoretical (upper) Raman spectra of $VO(NO_3)_3$.

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4.2.1. Case 1. One Nitrate Group with Monodentate Coordination and Two Nitrate Groups with Bidentate Coordination

The frequencies, infrared and Raman intensities and PED values obtained for this case by B3LYP calculations using 6-31G*, 6-311G* and 6-311+G* basis sets can be seen in Tables S7, S9 and S11. In all cases the theoretical values were compared with the respective experimental values by means of the RMSD values. The calculated harmonic force field for vanadyl nitrate can be obtained upon request. The frequencies calculated using the 6-31G* basis set for the compound in the 1800−1000 cm^{-1} region are higher than those obtained using the 6-311G* and 6-311+G* basis sets, but an inverse relation is observed at lower frequencies in the 1000−50 cm^{-1} region. The initial RMSD value using B3LYP/6-31G* calculation is 50.32 cm^{-1}, whereas with the 6-311G* and 6-311+G* basis sets the RMSD are 43.29 and 37.96 cm^{-1} respectively. Although the best results for vanadyl nitrate (see Table S6) are obtained with a B3LYP/6-311+G* calculation, the lower RMSD final value was obtained for the B3LYP/6-31G* level. In this case, the covalent bonding of the nitrate group is easily recognized in its infrared spectrum because the symmetry of the group decreases from the point group D_{3h} to C_s of the free ion for the compound [4, 38, 48].

Nitrate groups. The N=O stretching frequencies are observed between the 1672 and 1460 cm^{-1} regions [41−43, 45]. The band observed in the gas phase infrared spectrum of $VO(NO_3)_3$ at 1648 cm^{-1} and the shoulder in the infrared spectrum of the liquid compound at 1655 cm^{-1}, were assigned to N=O stretching in phase of the two equivalent nitrate groups (bidentate coordination). These bands in the Raman spectrum are polarized at 1659 cm^{-1}. The strong band observed in the liquid phase infrared spectrum of $VO(NO_3)_3$ at 1633 cm^{-1} is assigned to the corresponding N=O antisymmetric out of phase stretching. The N=O stretching frequencies of these modes are perfectly characterized with all basis sets and are underestimated in reference to the experimental values. Moreover, these modes are calculated with the three basis sets slightly coupled with the NO_2 stretching in phase modes.

Normally, the NO_2 antisymmetric modes are observed between 1488 and 1300 cm^{-1} [6, 42, 43, 45], whereas the symmetric modes are observed between 1364 and 1000 cm^{-1} [42, 43, 45]. In this case, the NO_2 antisymmetric frequencies, corresponding to a single nitrate group, lie in the mirror plane (monodentate coordination) and are calculated with all methods at higher frequencies than the other two equivalent nitrate groups. These modes appear to be coupled with O=N−O deformation modes in the same plane (Tables S7, S9 and S11). In the three theoretical calculations studied, the antisymmetric and symmetric modes are predicted with A′ symmetry. The shoulders in the gas spectrum at 1612 and 1216 cm^{-1} (the first band in the Raman spectrum appears as depolarized) are assigned to NO_2 antisymmetric and symmetric stretching modes, respectively.

In our previous paper [2], the NO_2 antisymmetric stretching in phase and out of phase modes of the two equivalent nitrate groups were assigned to two bands depolarized in the Raman spectrum at 1209 and 1196 cm^{-1} whereas the corresponding symmetric in phase and out of phase modes were assigned to the bands at 1006 and 997 cm^{-1}. In this case, the theoretical calculations predict both stretchings in phase and out of phase in the same frequency.

The N=O out of phase and in phase deformation modes, previously assigned at 994 cm^{-1} are well characterized by all calculations and moreover, they are predicted to be not coupled. The bands in the spectrum of vanadyl nitrate at 895 cm^{-1} and at 786 cm^{-1} in the spectrum in gas phase are assigned to in phase and out of phase deformation modes, respectively. The deformation mode corresponding to a nitrate group with monodentate coordination is observed coupled with the in phase deformation mode and reported in Table 4.

In general, the NO_2 out of phase and in phase deformation modes are observed between 831 and 433 cm^{-1} [6, 45]. In our previous paper, the bands in the Raman spectrum polarized at 789 cm^{-1} and the shoulder depolarized at 775 cm^{-1} were assigned to NO_2 in phase and out of phase deformation modes, respectively [2]. This last band is also assigned to the O=N−O deformation mode of the nitrate group with monodentate coordination wheras the band polarized in the Raman spectrum at 688 cm^{-1} is assigned to the NO_2 deformation mode of this nitrate group. Previously, we assigned the above band at 688 cm^{-1} in the Raman spectrum (very weak in the infrared) to the O−N=O bending modes. In this case, the O=N−O out of phase and in phase deformation modes are also coupled with the vibrations of nitrate groups and the V−O stretching as shown in Tables S7, S9 and S11. Here, the two modes are calculated at 691 and 676 cm^{-1} with the 6-31G* basis set whereas with the 6-311+G* basis set they are calculated at 699 and 685 cm^{-1}, respectively. In the nitrate ion O=N−O the out of phase deformation mode is observed at 831 cm^{-1} [6, 45] whereas in $UO_2(NO_3)_2$ it appears at 800 cm^{-1} [43]. The weak polarized band in the Raman spectrum at 688 cm^{-1} is also assigned to the O=N−O in phase deformation mode whereas the band in the infrared spectrum at 632 cm^{-1} is assigned to the out of phase mode.

In the region of lower frequencies, the N−O−V bending and twisting modes corresponding to covalent nitrates groups [43] are observed. As shown in Tables S7, S9 and S11, all modes appear coupled with other modes. The N−O−V bending mode is coupled with VO_2 vibration modes and is calculated at 226 cm^{-1} with the 6-31G* basis set, at 212 cm^{-1} with 6-311+G* basis set and at 221 cm^{-1} with 6-311G* basis set. Hence, the depolarized band at 238 cm^{-1} is assigned to the N−O−V bending mode.

Experimentally, the NO_2 twisting modes in nitro complexes are observed between 600 and 240 cm^{-1} [45]. These modes were not assigned in the previous paper [2]. In all calculations the NO_2 in phase torsion mode in vanadyl nitrate was calculated with a higher PED value but at lower

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frequencies than the corresponding out of phase mode. According to these observations, the bands in the infrared spectrum of the liquid phase at 133 and 93 cm^{-1} are assigned to NO_2 out of phase torsion and in phase modes, respectively. The depolarized band in the Raman spectrum at 192 cm^{-1} is clearly assigned to the NO_2 torsion mode corresponding to nitrate with monodentate coordination because it is well characterized in all calculations. As the calculation predicts, the Raman band at 110 cm^{-1} is assigned to N=O twisting of the monodentate nitrate group.

Vanadyl group. The V=O stretching mode is expected around 1000 cm^{-1} because in VOX_3 compounds like the tricarboxylates [49] or the trihalides [11, 50] it is observed in this region. In the calculations it is possible to observe the same differences between the three methods studied specially in the modes corresponding to the vanadyl group as shown in Tables S7, S9 and S11. In the B3LYP/6-31G* and B3LYP/6-311G* calculations the V=O stretching modes are predicted not coupled at 1151 and 1142 cm^{-1} as modes with A′ symmetry whereas with the B3LYP/6-311+G* level they are predicted at 1031 cm^{-1} but with A″ symmetry. Hence, the band at 1016 cm^{-1} is assigned to the V=O stretching mode. This mode originates a relatively strong band in the Raman spectrum, also characteristic of such compounds [11, 50]. Moreover being a mode of *A′* species, the corresponding band appears polarized in the Raman spectrum, as expected.

The metal-oxygen bands are expected in the 450−250 cm^{-1} region [41, 44]. In chromyl nitrate they appear at 457 (IR) and 446 cm^{-1} (Raman) [3, 37] with a separation of 11 cm^{-1}. This splitting should probably be larger for the bonds formed by the nitrate groups in the vanadyl compound. On this basis, the infrared bands located at 457 and 357 cm^{-1} (liquid) with counterparts having opposite relative intensities in the Raman spectrum (Table 5), are assigned to the V−O stretching modes of this group. In this work we confirm that the 303 cm^{-1} band is also due to these vibrations.

Table 5. Scale factors for the force field of vanadyl nitrate.

	[a]Vanadyl Nitrate					
	one nitrate monodentate			three nitrate bidentate		
Coordinates	6-31G*	6-311++G*	6-311G*	6-31G*	6-311++G*	6-311G*
ν (N=O)	0.875	0.918	0.894	0.875	0.919	0.893
ν (N−O)	0.902	0.964	0.949	0.904	0.964	0.946
ν (V=O)	0.773	0.778	0.785	0.772	0.778	0.785
ν (V−O)	1.054	1.080	1.041	1.058	1.102	1.056
δ (O=N=O)	0.979	0.949	0.954	0.976	0.946	0.946
δ (O−N−O)	0.979	0.949	0.954	0.976	0.946	0.946
δ (O=N−O)	0.979	0.949	0.954	0.976	0.946	0.946
δ (O=V−O)	1.037	1.095	1.028	1.041	1.084	1.030
δ (O−V−O)	0.968	1.002	0.974	0.978	1.008	0.985
δ (V−O−N)	0.979	0.949	0.954	–	–	–
τ (O−N−O)	0.972	1.098	0.945	0.967	0.993	0.944
γ (N=O)	1.190	1.157	1.075	1.191	1.158	1.171

ν = stretching, δ = deformation, ρ = rocking, wag (γ) = wagging, τw = torsion. [a] This work; * A single nitrate group lies in the mirror plane

The bending and rocking modes of the VO_2 group are not assigned in our previous paper [2]. In this case, the calculations predict these modes in the low frequencies region and coupled with other modes of the nitrate groups. The polarized band in the Raman spectrum at 285 cm^{-1} is assigned to both modes. The remaining VO_2 bending modes are assigned at 158, 110 and 59 cm^{-1} because they appear with higher PED values at lower frequencies (see Tables S7, S9 and S11).

4.2.2. Case 2. Three Nitrate Groups with Bidentate Coordination

The frequencies, infrared and Raman intensities and potential energy distribution obtained for this case by B3LYP calculations using 6-31G*, 6-311G* and 6-311+G* basis sets can be seen in Tables S8, S10 and S12 of the Supporting Material. In all cases the theoretical values were compared with the respective experimental values by means of the RMSD values. The lower RMSD final value for vanadyl nitrate was obtained with B3LYP/6-31G* and B3LYP/6-311+G* calculations. The calculated harmonic force field for vanadyl nitrate can be obtained upon request. The assignment of vanadyl nitrate as formed by three nitrate groups with bidentate coordination is practically the same as the one nitrate group in the above treatment. In this case, the nitrate groups were also considered as a four membered ring.

Nitrate groups. When the coordination mode adopted by nitrate groups is bidentate, the theoretical results show slight changes in the PED values and in the coupling of the modes. In this case, by using the three basis sets, the N=O stretching in phase modes appear to be coupled with the NO_2 in phase symmetric stretching mode, whereas the corresponding out of phase modes are also coupled with the NO_2 out of phase symmetric stretching. The assignment of both N=O stretchings are the same as presented above. In the higher frequency region, the only difference is the N=O stretching of the single nitrate group that lies in the mirror plane. This mode appears at 1612 cm^{-1}.

The NO_2 antisymmetric stretching of the single nitrate group that lies in the mirror plane is assigned clearly at 1216 cm^{-1} whereas the corresponding symmetric stretching is assigned at 965 cm^{-1} because these modes are well characterized by all calculations. The band in the vanadyl nitrate spectrum at 895 cm^{-1} is assigned to out of plane deformation mode corresponding to nitrate group in the position mentioned above as observed in Table 5.

Vanadyl group. Among the three methods it is possible to observe the same differences especially studied in the modes corresponding to vanadyl group as it is shown in Tables S8, S10 and S12. Here, in the three calculations there are differences in the position of the V=O stretching mode. When the 6-31G* and 6-311G* basis sets are used, the V=O stretching mode is predicted with higher PED values and not coupled as modes with A′ symmetry at 1151 and 1142 cm^{-1}, whereas in the calculation with 6-311+G* basis

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set the corresponding mode is also predicted with higher PED value and not coupled but with A″ symmetry at 1031 cm^{-1}. We assigned the polarized band in the Raman spectrum at 1016 cm^{-1} to the V=O stretching mode.

Other differences in the theoretical results can be seen in the V−O antisymmetric and symmetric stretching modes of the single nitrate group that lies in the mirror plane. In the three methods used both modes are predicted coupled among them and with other modes, such as the V−O stretching and the VO_2 bending of the other two equivalent nitrate groups localized in the perpendicular plane. Both V−O stretching modes are calculated with higher PED values and A′ symmetry respectively, at 226, 211 and 221 cm^{-1} using B3LYP/6-31G*, B3LYP/6-311+G* and B3LYP/6-311G* calculations. The V−O antisymmetric modes are calculated with the three methods with lower PED values (A″ symmetry). Hence, we assigned the intense polarized band in the Raman spectrum at 357 cm^{-1} to the symmetrical mode and the depolarized band in the same spectrum at 285 cm^{-1} to the antisymmetrical mode. The remaining V-O modes are easily assigned because with all methods with higher are calculated PED values.

In this case the six VO_2 bending (O=V−=O) modes expected are easily assigned with calculations although they are coupled with other modes in all methods used. The polarized band in the Raman spectrum at 285 cm^{-1} is assigned as case 1 to the VO_2 bending and rocking modes.

Summary

Comparing both coordination modes as can be seen in Tables S7 to S12, the SQM frequencies are practically the same with all methods. Observing the PED values obtained with the three methods, we note important differences between both coordination modes. Thus, for the B3LYP/6-31G* calculations (Tables S7 and S8), there are 17 of the 36 vibration modes that have the same PED contributions whereas in the case of three bidentate nitrate groups, only 15 normal modes have PED contributions higher than the other coordination mode (13 normal modes of A′ symmetry and only 2 normal modes of A″ symmetry). For the B3LYP/6-311+G* calculations considering three bidentate nitrate groups (Tables S9 and S10), there are 16 of the 36 vibration modes that have the same PED contributions and 17 normal modes with higher PED contributions than the other coordination modes. Finally, considering the B3LYP/6-311G* calculations (Tables S11 and S12) and three bidentate nitrate groups, 16 of the 36 expected modes have the same PED values and only 15 normal modes have higher PED contributions than the other coordination modes. For these observations, in spite the infrared spectroscopy is limited to determine the coordination mode of nitrate, we think that by means the GVFF study and the higher PED contributions are possible to justify the coordination mode of the nitrate group. In this case, for all studied methods a higher PED contribution is obtained for the compound considering three nitrate groups with bidentate coordination in its structure.

5. Force Field

The corresponding force constants were estimated by using the scaling procedure of *Pulay* et al. [23], as mentioned before. The harmonic force field in cartesian coordinates were transformed to the local symmetry or "natural" coordinates proposed by *Fogarasi* et al. [26] as defined in Tables S1 and S2 (see Figure 5 and Figure 6). The scaling factors affecting the main force constants were subsequently calculated by an iterative procedure [24, 25] in order to have the best possible fit between the observed and theoretical frequencies. In order to minimize the number of different scaling factors, those which are having similar values were unified. The resulting numbers for the three cases considered are collected in Table 5. These values are quite satisfactory with the three methods studied, considering that the experimental frequencies were not corrected for anharmonicity. The frequencies, infrared and Raman intensities and PED obtained for vanadyl nitrate appear together with the values reached for the corresponding RMSD values in Tables S7 to S12, for the two cases here considered for vanadyl nitrate. The force constants appearing in Table 6, expressed in terms of simple valence internal coordinates were calculated from the corresponding scaled force fields by using the expression: $F_i = U^t \cdot F_s \cdot U$, where F_i is the force constants matrix in terms of simple valence internal coordinates, F_s is the force constant matrix in terms of natural coordinates, U is the orthogonal matrix relating the natural coordinates to the simple valence internal coordinates, and U^t is the transpose of the U matrix. The force constants showed a good agreement with the three methods used. Obviously, some values related specifically with a single nitrate group that lies in the mirror plane and with the V−O bond localized in that plane varies slightly when its coordination mode changes. Thus, the force constant values indicated in Table 6 as f(N=O*) and f(V−O*) are different in the two cases considered. The force constant value for the f(N=O*) is lower in the monodentate case than in the bidentate case because in the first case there are two N=O antisymmetric and symmetric stretchings. This variation is justified by the Wiberg index value of the O atoms involved in the two N=O bonds of the nitrate group, as it is observed in Table S4. The Wiberg index value of the O10 atom is lower with all basis sets used (1.9760 with 6-31G* basis set) than the O12 atom (2.1978 with 6-31G* basis set). Thus, when the bidentate coordination is considered there is a N=O stretching where the O12 atom is involved in the bond which increases the f(N=O*) force constant. For this reasons, the force constant value for N−O bond of the nitrate group with monodentate coordination (A single nitrate group that lies in the mirror plane) is expected to be slightly different from the bidentate coordination mode. Again, in this last case there are two NO_2 stretching modes (antisymmetric and symmetric) where the O atoms involved in the

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corresponding bonds are the O11 and O13 atoms. The values for the N=O stretching force constant agree with the reported value of 11.83 mdyn $Å^{-1}$ for N_2O compound [6] whereas it is different from the 14.51 mdyn·$Å^{-1}$ value reported for the N_2O_2 compound [6]. The structures of both compounds are different from vanadyl nitrate, being N_2O linear and N_2O_2 angular with a 90° O−N−N angle. The force constant values reported for KNO_3 by *Beattie* et al. [51] were: 9.26 mdyn·$Å^{-1}$ for N=O stretching; 6.72 mdyn·$Å^{-1}$ for N−O stretching; 1.54 mdyn·Å·rad^{-2} for O−N−O deformation and 1.54 mdyn·Å·rad^{-2} for O=N−O deformation. The force constant values reported by *Brintzinger* et al. [52] and *Hester* et al. [53] for the free anion (6.35 mdyn·$Å^{-1}$ for N−O stretching; 2.05 mdyn·$Å^{-1}$ for N−O/N−O stretching and 0.54 mdyn·Å·rad^{-2} for O−N−O deformation) are near the cited values by Topping for D_{3h} nitrate ion (6.5 mdyn·$Å^{-1}$ for N−O stretching; 2.05 mdyn·$Å^{-1}$ for N−O/N−O stretching and 0.54 mdyn·Å·rad^{-2} for O−N−O deformation) [54]. For chromyl nitrate, those force constant values for the bidentate type are near to the monodentate coordination [3]. The observed differences in the force constants for KNO_3 can be attributed to the calculations because in that compound they were carried out using three observed N-O stretching frequencies (1460, 1293 and 1031 cm^{-1}) and the C_{2v} bidentate model.

Table 6. Comparison of scaled internal force constants for vanadyl nitrate.

	[a]Vanadyl Nitrate					
	one nitrate monodentate			three nitrate bidentate		
Coordinates	6-31G*	6-311++G	6-311G*	6-31G*	6-311++G	6-311G*
f (N=O)	11.42	11.73	11.58	11.29	11.74	11.59
f (N=O)*	9.20	9.51	9.43	11.03	11.27	11.17
f (N−O)	6.07	6.22	6.15	6.08	6.23	6.15
f (N−O)*	5.12	5.11	5.06	6.18	6.35	6.27
f (V=O)	7.39	7.08	7.42	7.39	7.08	7.42
f (V−O)	1.57	1.54	1.55	1.57	1.57	1.57
f (V-O)*	2.51	2.53	2.54	1.45	1.39	1.43
f (O−N−O)	1.76	1.74	1.74	1.76	1.73	1.73
f (O−N−O)*	1.60	1.55	1.59	1.73	1.70	1.71
f (O=N−O)	1.20	1.20	1.21	1.20	1.20	1.20
f (O=V−O)	1.15	1.15	1.15	1.15	1.14	1.15
f (O−V−O)	0.75	0.79	0.80	0.75	0.79	0.80

Units are mdyn·$Å^{-1}$ for stretching and stretching/stretching interaction and mdyn·Å·rad^{-2} for angle deformations. [a] This work. * A single nitrate group lies in the mirror plane

In this case, the force constants of the V=O stretching are slightly higher in vanadyl nitrate (7.39 mdyn·$Å^{-1}$ using 6-31G* basis set) than in the $VO_2X_2^-$ anions (6.54 mdyn·$Å^{-1}$ using 6-311+G basis set) [9] and they are slightly smaller than the VOX_3 compound anions [10]. These observations are justified because in the $VO_2F_2^-$ and $VO_2Cl_2^-$ anions the two V=O stretchings are observed in both cases at approximately 968 cm^{-1}, whereas the only V=O stretching is observed in the VOF_3 at 1058 cm^{-1} (7.87 mdyn·$Å^{-1}$ using 6-31+G basis set) and in the $VOCl_3$ at 1042 cm^{-1} (7.73 mdyn·$Å^{-1}$ using 6-31+G basis set).

The force constants of the V−O stretching change with the coordination mode of the nitrate group, being greater when a single nitrate group that lies in the mirror plane has monodentate coordination. This fact is justified, because in the bidentate case, there are two V−O bonds (V←O10 and V−O13 bonds) and the first bond by topological analysis is very weak as can be seen in Table 3. Moreover experimentally, the V←O10 length bond is greater than V−O13 length bond. On the other hand, in the monodentate case only the V−O13 is stronger than the other V−O bonds (see Table 3).

The analysis of the force constants suggests that the coordination that better represents the single nitrate group that lies in the mirror plane in vanadyl nitrate is the bidentate coordination because the obtained results are in accordance with the corresponding structure. Thus, for a single nitrate group the two N=O* stretching modes cannot have the same symmetry as the calculations predict; hence the calculated force constants for the only N=O* stretching mode with A′ symmetry has a reasonable value as for a bidentate coordination. Moreover, the force constants *f*(N=O*) values with all used methods cannot have lowest values (ca. 9.20 mdyn·$Å^{-1}$, B3LYP/6-31G* level) for a compound with two N=O* stretching that for a bidentate coordination (11.03 mdyn·$Å^{-1}$, B3LYP/6-31G* level). On the other hand, the force constants *f*(V−O*) values, for one V−O* stretching cannot have highest values (2.51 mdyn·$Å^{-1}$, B3LYP/6-31G* level) than the corresponding to a bidentate coordination (1.45 mdyn·$Å^{-1}$, B3LYP/6-31G* level).

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6. Conclusions

The assignments previously made [2] were confirmed and completed in accordance with the present theoretical results. The assignments of the 36 normal modes of vibration corresponding to vanadyl nitrate are reported. An approximate normal coordinate analysis considering the mode of coordination adopted by a single nitrate group that lies in the mirror plane as monodentate and bidentate was proposed. The method that best reproduces the experimental vibrational frequencies, considering the two coordination types of the nitrate group that lies in the mirror plane for vanadyl nitrate, is the B3LYP/6-31G*. The NBO and AIM analysis confirm the heptacoordination of the V atom in vanadyl nitrate.

We employed the 6-31G*, 6-311G* and 6-311+G* basis sets at the B3LYP level to obtain a molecular force field and vibrational frequencies. An SQM force field was obtained for vanadyl nitrate after adjusting the theoretically obtained force constants in order to minimize the difference between observed and calculated frequencies. We demonstrate that a DFT molecular force field for the vanadyl nitrate with the coordination mode adopted by the nitrate groups as bidentate, computed using 6-31G*, 6-311++G* and 6-311G* basis sets, are well represented.

Supporting information available: Tables S1−S12.

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DFT Calculations of the Molecular Force Field of Vanadyl Nitrate, $VO(NO_3)_3$