

## AB INITIO STUDY OF THE VIBRATIONAL SPECTRA OF NO<sub>3</sub>

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The vibrational spectra and geometry of the NO<sub>3</sub> molecule is studied using ab initio SCF and CASSCF methods. For all levels of theory and basis set the highest symmetry found is C<sub>2v</sub>. Vibrational levels agree well with recent experimental results.

### 1. Introduction

As an intermediate in atmospheric conversion involving oxides of nitrogen and ozone in both the stratosphere and troposphere, the nitrate radical, NO<sub>3</sub>, is one of the important molecules in atmospheric chemistry. However, the electronic and molecular structures of nitrate radical are not well characterized. The difficulty associated with experimental studies of its structure lies mainly in the diffuseness of the visible spectrum, either in absorption or fluorescence, due to extensive vibronic (Douglas) coupling. In 1983, Nelson et al. [1] and Ishiwata [2] independently obtained a laser-induced fluorescence spectrum of NO<sub>3</sub>, showing about 10 vibrational bands. The former group favored an assignment of C<sub>2v</sub> symmetry and the latter D<sub>3h</sub>. Neither group could assign all the bands in the spectrum. In 1985, Ishiwata et al. [3] deduced that NO<sub>3</sub> has D<sub>3h</sub> symmetry from an analysis of the vibrational band of the IR spectrum around 1490 cm<sup>-1</sup>. Although several anomalies accompanied their analysis, it was generally accepted that the equilibrium geometry of NO<sub>3</sub> has D<sub>3h</sub> symmetry. Later in 1986 Ishiwata et al. found evidence [4] that the band at 1490 cm<sup>-1</sup> was an electronic transition of either <sup>2</sup>A<sub>2</sub>' to <sup>2</sup>E'' or <sup>2</sup>A<sub>2</sub>' to <sup>2</sup>E'. From the analysis of the high resolution Fourier transform (FT) IR spectrum, which they fitted to D<sub>3h</sub> symmetry, Friedl and Sander [5] obtained similar results to those of Ishiwata [4]. Also they suggested the possible existence of a very-low-lying elec-

tronic excited state around 100 cm<sup>-1</sup> above the ground state.

Few theoretical studies have been done in which the geometry has been optimized for NO<sub>3</sub> [6-11]. Except for the work of Lund and Thuomas, who reported D<sub>3h</sub> symmetry with an NO distance of 1.240 Å, no other studies reported an absolute minimum at a geometry of D<sub>3h</sub> symmetry.

One motivation for this study was to obtain theoretical guidance in interpreting laser-induced fluorescence data that we have obtained [12] which suggest a C<sub>2v</sub> geometry. Meanwhile two recent theoretical studies have provided some vibrational frequencies [13,14]. The present study examines the equilibrium geometry and vibrational frequencies using ab initio self-consistent field (SCF) and complete-active-space SCF (CASSCF) analytic derivatives with no assumption of symmetry.

### 2. Computational methods and wavefunctions

Energies, optimized geometries, and vibrational frequencies have been obtained from restricted-open-shell Hartree-Fock (ROHF) and CASSCF treatments. The basis sets used are the double-zeta quality STO 4-31G basis set of Pople et al. [15] (DZ), the Dunning double-zeta [16] basis set augmented by polarization functions  $\alpha_d(\text{N})=0.8$  and  $\alpha_d(\text{O})=0.85$  (DZP), and a triple-zeta quality basis of Huzinaga and Dunning [16] (9s5p/5s3p) plus the same polarization functions (TZP). Geometries

Table 1  
Optimized geometries <sup>a)</sup> and harmonic vibrational frequencies <sup>b)</sup> for NO<sub>3</sub>

	ROHF			CASSCF	
	DZ	DZP	TZP	DZ	DZP
$R_{\text{NO}}(\text{long})$	1.406	1.339	1.432	1.420	1.342
$R_{\text{NO}}(\text{short})$	1.200	1.181	1.176	1.214	1.210 <sup>c)</sup>
$O_1\text{NO}_{2,3}$	114.5	114.3	114.1	114.8	113.92 <sup>d)</sup>
$\nu_1(a_1)$	932.7	1128.7	1111.9	928.3	1094.4
$\nu_2(a_1)$	1388.0	1594.3	1561.5	1353.1	1503.3
$\nu_3(a_1)$	665.4	741.5	738.4	662.5	703.8
$\nu_4(b_1)$	778.7	875.3	883.9	663.4	801.8
$\nu_5(b_2)$	1627.1	1888.1	1864.4	1799.0	1810.2
$\nu_6(b_2)$	548.9	592.6	595.2	519.8	577.4

<sup>a)</sup> Distances given in Å. <sup>b)</sup> Frequencies in cm<sup>-1</sup>.

<sup>c)</sup> C<sub>s</sub> geometry, the other bond length is 1.193 Å. <sup>d)</sup> C<sub>s</sub> geometry, the other bond angle is 114.9°.

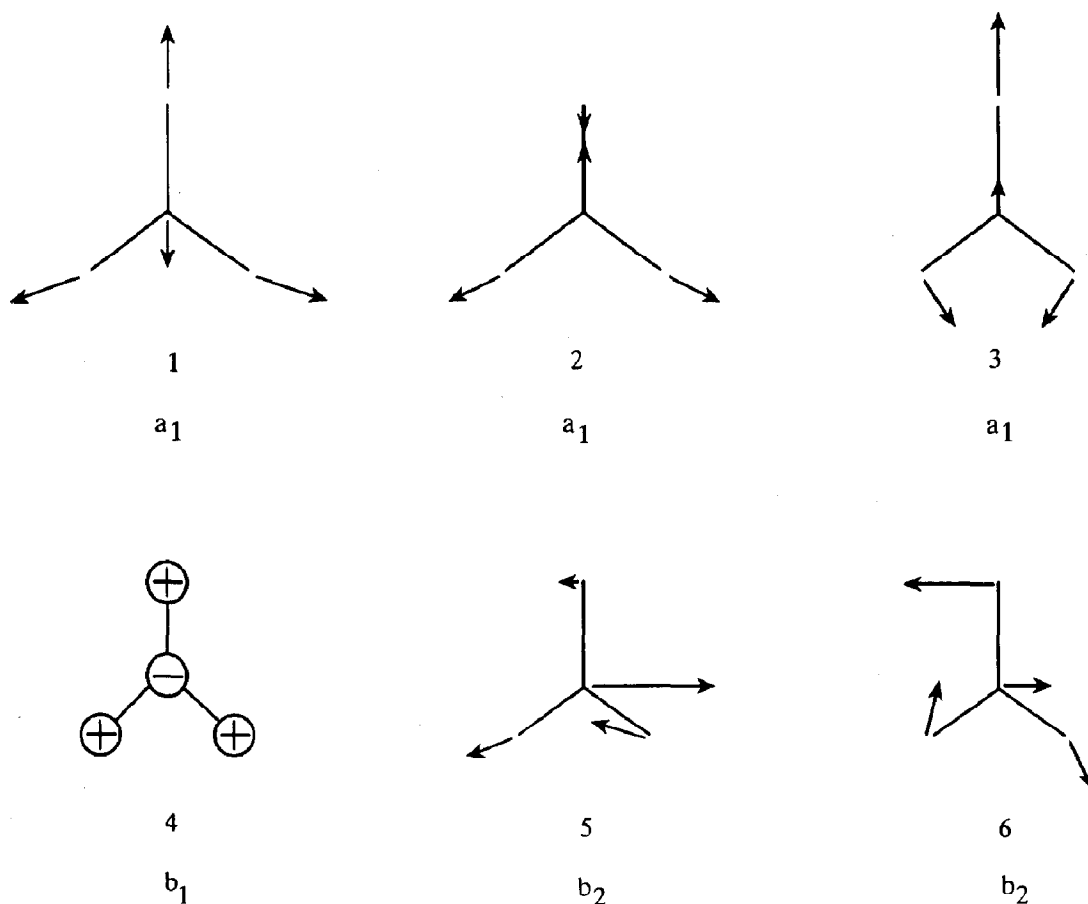


Fig. 1. Normal vibrations of NO<sub>3</sub>.

were optimized using analytic gradients, without symmetry restrictions, and vibrational frequencies were calculated within the harmonic approximation by a two-point finite difference of the analytic gradients. For the ROHF wavefunctions care was taken to converge to the proper  ${}^2B_2$  ground state of  $NO_3$ . We note that the unrestricted Hartree-Fock (UHF) treatment typically used for open-shell systems incorrectly predicts the ground state to have  ${}^2A_2$  symmetry, and is thus unreliable for this system. In our CASSCF study we have included only those orbitals necessary for the correct description of the radical wavefunction. Thus, for the DZ basis set the CAS included all excitations of the two electrons in the highest lying  $b_1$  (out-of-plane) and the unpaired  $b_2$  orbitals into  $b_1^*$  and  $a_1^*$  orbitals resulting in 20 configuration state functions. For the DZP basis results we have included excitation of an additional pair of electrons from the highest  $a_1$  orbital resulting in 75 configurations.

### 3. Results and discussion

In table 1 we present the total energies, optimized

geometries, and harmonic vibrational frequencies of  $NO_3$  for the ROHF and CASSCF wavefunctions described above. The normal modes of  $NO_3$  are shown in fig. 1. For all wavefunctions except the CASSCF DZP we have obtained an equilibrium geometry of  $C_{2v}$  symmetry. For the CASSCF DZP wavefunction we observe symmetry breaking to produce  $C_s$  symmetry. The problem of symmetry breaking in multi-configuration SCF is well studied [17], and has recently been addressed by Davy and Schaefer [13] for the  $NO_3$  molecule. Previous theoretical studies have obtained a variety of results with  $C_{2v}$  symmetry. Only Lund and Thuomas [8] obtained a  $D_{3h}$  minimum energy geometry, although Siegbahn's results suggest that  $D_{3h}$  might be the true minimum. Davy and Schaefer [13] have taken up the question of symmetry breaking in  $NO_3$ , using a CASSCF wavefunction including all 2s and 2p electrons on N and the 2p O electrons (a wavefunction with over 100000 configuration state functions) to obtain an acute isosceles triangle with bond lengths of 1.351 and 1.224, in good agreement with our best results. They conclude that either  $C_{2v}$  symmetry is the true minimum, or "the symmetry breaking problem [is] more difficult to overcome than previously thought"

Table 2

Comparison of experimental and theoretical geometries <sup>a)</sup> and harmonic vibrational frequencies <sup>b)</sup> for  $NO_3$

	MP2 <sup>c)</sup>	CASSCF <sup>d)</sup>	ROHF <sup>e)</sup>	CASSCF <sup>e)</sup>	Expt.	
	DZP $C_{2v}$	DZP $D_{3h}$	TZP $C_{2v}$	DZP $C_s$	LIF <sup>f)</sup> $C_{2v}$	FT IR <sup>g)</sup> $D_{3h}$
$R_{NO}(\text{long})$	1.337	1.256	1.342	1.342		1.24
$R_{NO}(\text{short})$	1.180	1.256	1.176	1.210 <sup>h)</sup>		1.24
$O_1NO_{2,3}$	114.2	120.0	114.1	113.92 <sup>i)</sup>		120.0
$\nu_1(a_1)$	1122	1068	1112	1094	1050	1060
$\nu_1^j$	9		8	6		
$\nu_2(a_1)$	1590	963	1562	1503	1498	1492
$\nu_2^j$	27		27	34		
$\nu_3(a_1)$	741		738	704	749	762
$\nu_3^j$	1		1	2		
$\nu_4(b_1)$	877		884	802	366	
$\nu_4^j$	4		3	3		
$\nu_5(b_2)$	2005		1864	1810	2008	
$\nu_5^j$	100		100	100		
$\nu_6(b_2)$	686		595	577	775	380
$\nu_6^j$	1		1	1		

<sup>a)</sup> Distance given in Å. <sup>b)</sup> Frequencies in  $cm^{-1}$ . <sup>c)</sup> Ref. [14]. <sup>d)</sup> Ref. [13]. <sup>e)</sup> This work. <sup>f)</sup> Ref. [12]. <sup>g)</sup> Refs. [3,5].

<sup>h)</sup>  $C_s$  geometry, the other bond length is 1.193 Å. <sup>i)</sup>  $C_s$  geometry, the other bond angle is  $114.9^\circ$ . <sup>j)</sup> IR intensity normalized to  $\nu_5 = 100$ .

[13]. Thus we feel secure that our predicted geometry will not adversely affect our vibrational frequency calculations.

In table 2 we compare vibrational frequencies obtained by various theoretical and experimental approaches. The vibrational frequencies determined from both our ROHF and CASSCF computations are compared with the tentative interpretation of our laser-induced fluorescence data [12]. The main vibrational complication in this system is that the  $D_{3h}$  structure represents a low barrier to vibration among multiple minima. The harmonic frequencies reported here do not account for the possibility of strong anharmonic couplings.

The calculated IR intensities of each band are also listed in table 2. The intensities have been adjusted so that the strongest absorption, the asymmetric stretch at  $1810\text{ cm}^{-1}$ , is 100. One reason for the previous experimental assignments of  $D_{3h}$  symmetry has been the absence of a band around  $1050\text{ cm}^{-1}$  [5], a band forbidden by  $D_{3h}$  symmetry. The calculated IR intensities indicate that the intensity of this transition is weak. A fruitful approach might be a study of the  $b_2$  asymmetric stretch mode, the strongest calculated absorber, which has not been reported elsewhere [1-5].

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