NO3 full-dimensional potential energy surfaces and ground state vibrational levels revisited

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Abstract

A new full-dimensional (6D) diabatic potential energy surface (PES) model is presented representing the five lowest PESs corresponding to the $\tilde{X}^2A_2'$, $\tilde{A}^2E''$, and $\tilde{B}^2E'$ electronic states of the nitrate radical (NO_3). It is based on high-level *ab initio* calculations of roughly 90 000 energy data over a wide range of nuclear configurations and represents the energies with a root mean-squares (rms) error of about 100 cm^{-1}. An accurate dipole surface was developed for the $\tilde{X}$ state as well. The new PES model is used to re-investigate the infra-red (IR) spectrum corresponding to the electronic ground state by full quantum dynamics simulations. Vibrational eigenstates, IR transition probabilities, and isotopic shifts are computed and analyzed. Levels up to 2000 cm^{-1} are obtained and show good to excellent agreement with known experimental values. Some larger deviations are observed and discussed as well. The new results are in agreement with previous theoretical studies that the disputed ν_3 fundamental corresponds to a frequency of roughly 1022 cm^{-1} and that the prominent experimental feature observed at 1492 cm^{-1} is due to the 3^14^1 (e') combination mode. Observed discrepancies in the IR intensities may be explained by coupling to the $\tilde{B}$ state which is also analysed by diabatic decomposition of the eigenstates.

1. Introduction

NO_3, one of the first known free radicals, is the subject of intense research and lively controversy still more than 130 years after its first discovery[1] and almost 90 years after its first spectroscopic characterization[2]. A number of idiosyncrasies have sparked the interest of experimentalists and theoreticians alike - besides its high relevance in atmospheric chemistry.[3, 4] Three electronic states are known to date, the $^2A_2'$ ground state, the first excited state of $^2E''$ symmetry, and the second excited state of $^2E'$ symmetry. The $\tilde{B}$ state absorbs strongly in the visible and has been measured as early as in the 1930s.[2, 5, 6] This state is subject to

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photodissociation though it shows a long life-time at the same time.[7, 8, 9, 10, 11] The $\tilde{A}$ state is difficult to observe in direct absorption because transitions are formally dipole-forbidden. However, it has been observed first by photodetachment spectroscopy from the anion.[12] Much later it was measured by cavity ring-down spectroscopy in a number of studies.[13, 14, 15, 16] This state also has been observed in neon matrices at 4.3 K.[17] The analysis of these spectra is still under way. Finally, the $\tilde{X}$ state can be readily studied by a number of high-resolution spectroscopic techniques. The vibrational and ro-vibrational levels have been studied by several groups with different techniques.[18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33] A lively debate has developed about the assignment of a feature around 1492 cm^{-1} caused by a theoretical study[34] proposing that this level may not be the ν_3 fundamental but a 1^14^1 combination band. In a follow-up study, this theoretical assignment was corrected to 3^14^1 [57].

The theoretical treatment of NO_3 has been no less controversial due to intrinsic problems of the electronic structure. There has been a long debate about the equilibrium geometry, C_{2v} vs. D_{3h},[35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45] and finally it could be shown that the distorted C_{2v} geometries are due to artificial symmetry-breaking of the electronic wave function.[46] A comprehensive discussion of this can be found in ref. [46, 47]. A further controversy was the question whether or not a stable isomer ONOO (peroxy nitrate) exists. Its existence at least as intermediate has been proposed by several groups based on experiment and theory.[48, 49, 50, 51, 40] The experimental evidence turned out to be due to systematic errors.[52] Finally, we could show that the theoretical support for a stable ONOO isomer was also due to inappropriate use of single-reference electronic structure methods.[53] Several quantum dynamics studies also appeared treating various spectroscopic aspects.[54, 14, 34, 55, 56, 57, 58, 59, 60, 61, 62] All except one of these studies utilize a vibronic coupling or diabatic representation of the electronic Hamiltonian to obtain an analytical potential energy surface (PES) model. We also present an accurate diabatic 5-state PES model in the present study which is an extension of our previous work.[61, 62]

The reason for using such a diabatic representation even for the ground state is the extreme anharmonicity in the corresponding PES which is due to strong couplings to the Jahn-Teller (JT) active excited $\tilde{B}$ state. The presence of conical intersections and the resulting breakdown of the Born-Oppenheimer (BO) approximation for the excited states renders such an approach very desirable.[63] The nuclear and electronic degrees of freedom are coupled in the excited states, which has to be accounted for in any reasonable theoretical treatment. By contrast, the electronic ground state could be treated adiabatically without any problems but the adiabatic PES is difficult to be fitted. This turns out to be much easier in the fully coupled diabatic representation.

The benefits of a diabatic or rather *quasi*-diabatic representation of the electronic Hamiltonian and corresponding PES matrix are well-known by now.[63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74] Though the linear vibronic coupling method has been tremendously successful,[75] it is also too limited to yield accurate PESs. For this reason we and others have been developing methods to diabatize electronic structure

data[76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90] and to generate and represent coupled PESs that are accurate over a large range of nuclear configurations. [91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108] We recently applied our methodology to the development of a highly accurate diabatic representation of the $^2E''$ first excited electronic state of NO_3, which is a prototypical Jahn-Teller system in which the proper treatment of the direct dissociation asymptotes is very important.[61] In the present study, we extend this PES model for a detailed analysis of the nuclear dynamics in the $\tilde{X}\ ^2A_2'$ state.

The paper is organized as follows. Section 2 provides a brief description of the diabatic PES model and the dipole surface model. Section 3 provides the technical and numerical details of the vibrational level computations. Results of the numerical simulations are given, analyzed, and discussed in detail in Section 4 and the conclusions of this work are summarized in Section 5.

2. Diabatic potential model

The electronic ground state $\tilde{X}\ ^2A_2'$ is non-degenerate and could be represented by a single adiabatic PES in principle. In fact, this has been done.[60] However, the $\tilde{X}$ state is coupled to the Jahn-Teller active $\tilde{B}$ state of $^2E'$ symmetry by a significantly strong *pseudo*-JT coupling as was first stated by Mayer *et al.*[54] and confirmed much later by Stanton.[34] This coupling has an effect on the shape of the ground state PES making it harder to represent the data as a single uncoupled PES. Furthermore, we are interested in the photo chemistry and absorption spectroscopy of NO_3 and both low-lying excited states, the $\tilde{A}\ ^2E''$ as well as the $\tilde{B}\ ^2E'$ state, are JT active with a conical intersection at D_{3h}/C_{3v} geometries. It is of great advantage to represent such a system in the diabatic electronic basis. Our aim is to develop a full-dimensional, global, and accurate diabatic model for all relevant electronic states of this complicated system. So far the diabatic treatment of NO_3 was mostly restricted to the simple linear and quadratic vibronic coupling approach.[54, 34, 58] We extended this treatment to higher order JT couplings[100, 101] and global PESs step by step first for the isolated $^2E''$ state and used that system for the development of our methodology.[55, 56, 61]

Here we extend our approach to the diabatic representation of the three lowest electronic states of NO_3 including five state components and thus yielding a 5×5 diabatic PES matrix depending on the six nuclear coordinates Q_i. The diabatic electronic basis states are used in the order $|^2A_2'\rangle$, $|^2E_x''\rangle$, $|^2E_y''\rangle$, $|^2E_x'\rangle$, and $|^2E_y'\rangle$ in the following. This yields the diabatic matrix

$$\boldsymbol{E}^d(\boldsymbol{Q}) = \begin{pmatrix} \mathcal{V}_{\tilde{X}}(\boldsymbol{Q}) & 0 & 0 & 0 & 0 \\ 0 & \mathcal{V}_{\tilde{A}}(\boldsymbol{Q}) & 0 & 0 & 0 \\ 0 & 0 & \mathcal{V}_{\tilde{A}}(\boldsymbol{Q}) & 0 & 0 \\ 0 & 0 & 0 & \mathcal{V}_{\tilde{B}}(\boldsymbol{Q}) & 0 \\ 0 & 0 & 0 & 0 & \mathcal{V}_{\tilde{B}}(\boldsymbol{Q}) \end{pmatrix} \tag{1}$$

$$
+\begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & \mathcal{W}_{\tilde{A}}(\boldsymbol{Q}) & \mathcal{Z}_{\tilde{A}}(\boldsymbol{Q}) & 0 & 0 \\
0 & \mathcal{Z}_{\tilde{A}}(\boldsymbol{Q}) & -\mathcal{W}_{\tilde{A}}(\boldsymbol{Q}) & 0 & 0 \\
0 & 0 & 0 & \mathcal{W}_{\tilde{B}}(\boldsymbol{Q}) & \mathcal{Z}_{\tilde{B}}(\boldsymbol{Q}) \\
0 & 0 & 0 & \mathcal{Z}_{\tilde{B}}(\boldsymbol{Q}) & -\mathcal{W}_{\tilde{B}}(\boldsymbol{Q})
\end{pmatrix}
$$

$$
+\begin{pmatrix}
0 & \mathcal{W}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) & -\mathcal{Z}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) & \mathcal{W}_{\tilde{X}\tilde{B}}(\boldsymbol{Q}) & -\mathcal{Z}_{\tilde{X}\tilde{B}}(\boldsymbol{Q}) \\
\mathcal{W}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) & 0 & 0 & \mathcal{V}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) + \mathcal{W}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & \mathcal{Z}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) \\
-\mathcal{Z}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) & 0 & 0 & \mathcal{Z}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & \mathcal{V}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) - \mathcal{W}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) \\
\mathcal{W}_{\tilde{X}\tilde{B}}(\boldsymbol{Q}) & \mathcal{V}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) + \mathcal{W}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & \mathcal{Z}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & 0 & 0 \\
-\mathcal{Z}_{\tilde{X}\tilde{B}}(\boldsymbol{Q}) & \mathcal{Z}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & \mathcal{V}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) - \mathcal{W}_{\tilde{A}\tilde{B}}(\boldsymbol{Q}) & 0 & 0
\end{pmatrix}
$$

in which the functions $\mathcal{V}$, $\mathcal{W}$, and $\mathcal{Z}$ are symmetry-adapted power expansions in terms of symmetry-adapted nuclear coordinates. The corresponding expansion coefficients are determined by the diabatization approach utilizing computed electronic structure data (see below). The basic symmetry monomials have been derived by us and others before and need not to be repeated here.[100, 101, 61] For the present work we included all terms up to fourth order including all possible multi-mode couplings. Special attention has to be paid to the symmetry-breaking umbrella coordinate Q_2 which transforms as a_2''. Only monomials with odd powers Q_2^{2n+1} are allowed in the coupling functions $\mathcal{W}_{\tilde{X}\tilde{A}}$, $\mathcal{Z}_{\tilde{X}\tilde{A}}$, $\mathcal{V}_{\tilde{A}\tilde{B}}$, $\mathcal{W}_{\tilde{A}\tilde{B}}$, and $\mathcal{Z}_{\tilde{A}\tilde{B}}$. All other functions must only contain monomials with even powers Q_2^{2n} of this coordinate.

The coordinates are constructed from a set of primitive valence coordinates. These are the three N–O distances, an umbrella angle θ defined as the angle of any of the N–O bonds to the plane normal to the trisector, which is a line in space going through the central N atom to which all three N–O bonds form the same angle, and the three O–N–O angles obtained from projection of the N–O bonds onto the normal plane corresponding to the trisector.[61] Then the three N–O distances are transformed first into displacements Δr_i with respect to the equilibrium distance r_e of the ground state and then into Morse coordinates

$$
m_i(\Delta r_i) = 1 - e^{-\alpha \Delta r_i}, \qquad i = 1, 2, 3. \tag{2}
$$

These Morse coordinates are symmetry-adapted by the well known point-group Clebsch-Gordan coefficients for D_{3h} to yield the a_1' totally symmetric stretch and a set of e' asymmetric stretch coordinates:

$$
\begin{pmatrix} Q_1 \\ Q_3 \\ Q_4 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} m_1 \\ m_2 \\ m_3 \end{pmatrix}. \tag{3}
$$

The three projected O–N–O angles are first divided by the product of the two N–O distances forming the scaled angles

$$
\tilde{\alpha}_i = \frac{\alpha_i}{r_j r_k}, \qquad i \neq j \neq k \in \{1, 2, 3\} \tag{4}
$$

and then symmetry-adapted exactly like the distances

$$\begin{pmatrix} Q_5 \\ Q_6 \end{pmatrix} = \begin{pmatrix} \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}. \tag{5}$$

The totally symmetric linear combination is discarded because it is an inappropriate coordinate. The above defined umbrella angle is used instead, which is scaled by the N–O distances as

$$Q_2 = \theta \, \frac{r_e^3}{r_1 r_2 r_3}. \tag{6}$$

To give an idea how the diabatic PES functions of eq. (1) actually look like, we present explicitly the two dynamic *pseudo*-JT coupling elements $\mathcal{W}_{\tilde{X}\tilde{A}}$ and $\mathcal{Z}_{\tilde{X}\tilde{A}}$ in terms of the above coordinates, which read

$$\begin{aligned} \mathcal{W}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) = \quad & p_1^{(1)} Q_2 \\ & + p_1^{(2)} Q_2 Q_3 + p_2^{(2)} Q_2 Q_5 + p_3^{(2)} Q_1 Q_2 \\ & + p_1^{(3)} Q_2^3 + p_2^{(3)} Q_2 (Q_3^2 - Q_4^2) + p_3^{(3)} Q_2 (Q_5^2 - Q_6^2) + p_4^{(3)} Q_2 (Q_3 Q_5 - Q_4 Q_6) \\ & + p_5^{(3)} Q_1 Q_2 Q_3 + p_6^{(3)} Q_1 Q_2 Q_5 \\ & + p_1^{(4)} Q_2 (Q_3^3 + Q_3 Q_4^2) + p_2^{(4)} Q_2 (Q_5^3 + Q_5 Q_6^2) + p_3^{(4)} Q_2 (Q_3^2 Q_5 + Q_4^2 Q_5) \\ & + p_4^{(4)} Q_2 (Q_3 Q_6^2 + Q_3 Q_5^2) + p_5^{(4)} Q_2 (2 Q_3 Q_4 Q_6 + Q_3^2 Q_5 - Q_4^2 Q_5) \\ & + p_6^{(4)} Q_2 (Q_3 Q_5^2 + 2 Q_4 Q_5 Q_6 - Q_3 Q_6^2) + p_7^{(4)} Q_1 Q_2 (Q_3^2 - Q_4^2) + p_8^{(4)} Q_1 Q_2 (Q_5^2 - Q_6^2) \\ & + p_9^{(4)} Q_1 Q_2 (Q_3 Q_5 - Q_4 Q_6) + p_{10}^{(4)} Q_1^2 Q_2 Q_3 + p_{11}^{(4)} Q_1^2 Q_2 Q_5 + p_{12}^{(4)} Q_1 Q_2^3 \\ & + p_{13}^{(4)} Q_2^3 Q_3 + p_{14}^{(4)} Q_2^3 Q_5 \end{aligned} \tag{7}$$

and

$$\begin{aligned} \mathcal{Z}_{\tilde{X}\tilde{A}}(\boldsymbol{Q}) = \quad & p_1^{(1)} Q_2 \\ & + p_1^{(2)} Q_2 Q_4 + p_2^{(2)} Q_2 Q_6 + p_3^{(2)} Q_1 Q_2 \\ & + p_1^{(3)} Q_2^3 - 2 p_2^{(3)} Q_2 Q_3 Q_4 - 2 p_3^{(3)} Q_2 Q_5 Q_6 - p_4^{(3)} Q_2 (Q_3 Q_6 + Q_4 Q_5) \\ & + p_5^{(3)} Q_1 Q_2 Q_4 + p_6^{(3)} Q_1 Q_2 Q_6 \\ & + p_1^{(4)} Q_2 (Q_3^2 Q_4 + Q_4^3) + p_2^{(4)} Q_2 (Q_5^2 Q_6 + Q_6^3) + p_3^{(4)} Q_2 (Q_4^2 Q_6 + Q_3^2 Q_6) \\ & + p_4^{(4)} Q_2 (Q_4 Q_6^2 + Q_4 Q_5^2) + p_5^{(4)} Q_2 (Q_4^2 Q_6 + 2 Q_3 Q_4 Q_5 - Q_3^2 Q_6) \\ & + p_6^{(4)} Q_2 (Q_4 Q_6^2 + 2 Q_3 Q_5 Q_6 - Q_4 Q_5^2) - p_7^{(4)} 2 Q_1 Q_2 Q_3 Q_4 - p_8^{(4)} Q_1 Q_2 Q_5 Q_6 \\ & - p_9^{(4)} Q_1 Q_2 (Q_3 Q_6 + Q_4 Q_5) + p_{10}^{(4)} Q_1^2 Q_2 Q_4 + p_{11}^{(4)} Q_1^2 Q_2 Q_6 + p_{12}^{(4)} Q_1 Q_2^3 \\ & + p_{13}^{(4)} Q_2^3 Q_4 + p_{14}^{(4)} Q_2^3 Q_6. \end{aligned} \tag{8}$$

Note that both functions must share a common set of expansion parameters $p_j^{(n)}$ because these functions are strictly related by symmetry. The free parameters p in the diabatic functions need to be determined based

on accurate electronic structure calculations. The required energy data was computed at multi-configuration reference singles and doubles configuration interaction (MR-SDCI) level of theory using a modified triple-ζ basis. The technical details of the *ab initio* calculations can be found in refs. [46, 47] These calculations have been performed in two different sets, a large 5D set for planar geometries and a smaller 6D one including displacement of the umbrella coordinate. In order to detect potential convergence issues of the *ab initio* data, these calculations are performed along well-defined straight random cuts through the PESs as described in refs. [109, 61, 90] The free parameters are then obtained by a non-linear least squares fitting algorithm based on the Marquardt-Levenberg method incorporated into a genetic algorithm. The diabatization is achieved by the requirement that the eigenvalues of the diabatic model need to optimally reproduce the adiabatic energies for all nuclear configurations in the data set. The fit is first performed for the 5D data restricted to planar nuclear configurations. This first fitting step is based on 86 661 adiabatic energy data from the MRCI *ab initio* calculations. The obtained parameters are then frozen and a second fit with a set of full 6D data (3 034 energies) is performed only optimizing the parameters for terms including displacements in the umbrella coordinate. An exponential weighting of the data is applied with respect to the reference energies at the ground state equilibrium geometry in order to improve the representation of the most relevant regions of the PESs which are of lower energy. This approach yields an unweighted root mean-squares (rms) error of below 100 cm^{-1} for all energies up to 1 eV above the origin of each of the electronic states. The weighted rms error for all energies included into the fit spanning a range of several eV is only about 120 cm^{-1}, demonstrating the excellent representation of the electronic structure data over a large range of nuclear configurations.

Finally, we also need the dipole surfaces in order to compute IR intensities. For simplicity this is only done in the adiabatic approximation for the electronic ground state. It turns out that the widely applied linear approximation is insufficient in the case of the NO_3 ground state since strong multi-mode effects and non-linearity are present. A symmetry analysis of the three vector components of the dipole function $\vec{\mu}(\boldsymbol{Q})$ yields that it is properly represented in terms of the symmetry-adapted polynomials as

$$\vec{\mu}(\boldsymbol{Q}) = \begin{pmatrix} \mathcal{W}_\mu(\boldsymbol{Q}) \\ \mathcal{Z}_\mu(\boldsymbol{Q}) \\ Q_2^{2n+1}\, \mathcal{V}_\mu(\boldsymbol{Q}) \end{pmatrix}. \tag{9}$$

We find that μ_z hardly depends on any other coordinates except Q_2 and thus it is simply modeled by the linear and cubic term in Q_2. The other two components μ_x and μ_y show strong multi-mode effects and are expanded to full third order including all multi-mode terms in the $\mathcal{Z}$ and $\mathcal{W}$ functions. The 14 free parameters are fitted with respect to a total of 612 *ab initio* data in full 6D and a satisfactory representation of the data was achieved by the above model.

3. Computational Details

For the determination of the vibrational levels supported by the electronic ground state, we employed the MCTDH approach,[110, 111, 112] which is a powerful scheme to describe wave functions of large systems. $^{14}N^{16}O_3$ as well as two other isotopologues have been considered. The state average and block diagonalization scheme as described in ref. [113] is used to compute vibrational levels. In our previous work on the first excited state of NO_3 [62], we have shown that the six internal curvilinear coordinates as proposed in ref. [114] are convenient coordinates to describe NO_3. These six internal curvilinear coordinates $\rho^{(\mathrm{cu})}, \vartheta^{(\mathrm{cu})}, \varphi^{(\mathrm{cu})}, \theta^{(\mathrm{cu})}, \phi^{(\mathrm{cu})}, \chi^{(\mathrm{cu})}$ are based on the three Radau vectors of the AB_3 system. Planarity is given for $\theta^{(\mathrm{cu})} = \pi/2$ where $\theta^{(\mathrm{cu})}$ is defined as the angle between each of the Radau vectors and the trisector of the Radau vectors. The exact kinetic energy operator cannot be used directly in the MCTDH implementation due to the fact that one of the terms cannot be expressed as sum of products of single coordinate terms. As proposed in ref. [114], the fourth order Taylor expansion is used here. This approximation has been tested on the computation of NO_3^- vibrational and NO_3 vibronic energy levels [62] for which we tested an alternative set of coordinates, namely the stereographic coordinates as defined in ref. [115]. The differences are below 1 cm^{-1}.

These coordinates have indeed two qualities when studying NO_3. First, the quite physical nature of these coordinates ensures that for the eigenvector representations the correlation between the coordinates is moderate. The consequence is a faster convergence of the MCTDH scheme with respect to the number of single particle functions. Second and most importantly, when using this particular set of coordinates one can easily evaluate the effect of the symmetry operators of the C_{2v} subgroup of the relevant D_{3h} symmetry group. With the xy plane being the molecular plane, the σ_{xy} reflection acts on the $\theta^{(\mathrm{cu})}$ only around the $\pi/2$ symmetry point, the σ_{xz} reflection acts on both $\varphi^{(\mathrm{cu})}$ and $\chi^{(\mathrm{cu})}$ around the $\pi/4$ and the π symmetry point, respectively, and the C_2 rotation acts on the three $\theta^{(\mathrm{cu})}, \varphi^{(\mathrm{cu})}$ and $\chi^{(\mathrm{cu})}$ angles. The correlation between D_{3h} and C_{2v} irreducible representations and corresponding characters of the two C_{2v} reflections are given in Tab. 1.

Table 1: Relation between irreps in C_{2v} and D_{3h} within the orientational convention of this work. The characters with respect to the two σ_v reflection of C_{2v} are also provided for convenience.

$\Gamma_{D_{3h}}$	$\Gamma_{C_{2v}}$	$\sigma_v(xy)$	$\sigma_v(xz)$
$a_1^{'}$ or $e^{'}$	a_1	1	1
$a_2^{'}$ or $e^{'}$	b_1	1	-1
$a_1^{''}$ or $e^{''}$	a_2	-1	-1
$a_2^{''}$ or $e^{''}$	b_2	-1	1

Although the kinetic energy terms fulfill the sum of products of single particle constraint of operators to render the MCTDH approach most efficient, the potential term does not respect this requirement. Therefore,

when studying the vibrational levels supported by the adiabatic ground state, the evaluation of the single-state (or single-valued) potential term is carried out using the original CDVR scheme.[116] For the diabatic calculations employing the full 5×5 matrix operator the multi-state CDVR scheme is utilized.[102] Table 2 gives the basis set details, namely box range, underlying grid size N, and number of single particle functions n which have been converged in order to ensure numerical accuracy of the final results to better than one cm^{-1}.

Table 2: Wave function representations given by the number of single particle functions (n), the number of Fourier points (N) and the range of the underlying box [in a.u.] for the six curvilinear coordinates of hyperspherical type constructed using mass weighted Cartesian coordinates for $^{14}N^{16}O_3$, $^{15}NO_3$ and $^{14}N^{18}O^{16}O_2$.

	$^{14}N^{16}O_3$			$^{15}N^{16}O_3$			$^{14}N^{18}O^{16}O_3$		
coord.	n	N	range	n	N	range	n	N	range
$\rho^{(cu)}$	5	32	[648 : 753]	5	32	[648 : 753]	5	32	[645 : 765]
$\vartheta^{(cu)}$	7	32	[0.855 : 1.055]	7	32	[0.855 : 1.055]	7	32	[0.855 : 1.055]
$\varphi^{(cu)}$	7	32	[0.685 : 0.885]	7	32	[0.685 : 0.885]	7	32	[0.685 : 0.885]
$\theta^{(cu)}$	5	32	[1.471 : 1.671]	5	32	[1.471 : 1.671]	5	32	[1.471 : 1.671]
$\phi^{(cu)}$	9	32	[0.827 : 1.217]	9	32	[0.827 : 1.217]	9	32	[0.807 : 1.217]
$\chi^{(cu)}$	10	32	[2.741 : 3.541]	10	32	[2.741 : 3.541]	10	32	[2.741 : 3.541]

The vibrational energy levels are also computed in a complimentary way. A time-independent Hermite discrete variable representation (DVR) approach is used[117] and the corresponding Hamiltonian is diagonalized by an exact short iterative Lanczos method. Normal coordinates from an MRCI frequency calculation are used and vibrational angular momenta are ignored in the kinetic energy operator. Standard harmonic oscillator functions are chosen for the finite basis representation (FBR) and the kinetic energy is transformed into the corresponding DVR grid point basis. The six coordinates and their irreps in D_{3h} correspond to totally symmetric stretch (ν_1, a_1'), out-of-plane or umbrella bending (ν_2, a_2''), asymmetric stretch (ν_{3x}/ν_{3y}, e'), and asymmetric bend (ν_{4x}/ν_{4y}, e'), respectively. The associated numbers of basis functions/DVR grid points are 15, 14, 17, 17, 18, and 18, which yields total energies converged to better than 10^{-1} cm^{-1} when compared to a basis with one basis function less in each mode. The degeneracies are reproduced to better than 10^{-2} cm^{-1} for all degenerate levels. The diagonalization is carried out in the DVR basis and the resulting eigenvectors are transformed back into the FBR, in which the eigenstate composition can be analyzed conveniently in terms of vibrational quanta in each of the modes.

4. Results and Discussion

The eigenstates of three isotopologues of the NO_3 $\tilde{X}$ state supported by the lowest adiabatic potential of the new diabatic PES model are collected in Tabs. 3, 4 and 5. These computations were carried out by both the time-dependent MCTDH approach and the time-independent DVR method to gain a maximum of information. The obtained energies are in close agreement and the observed minor differences originate

from the more approximate kinetic energy used for the DVR calculations. Therefore, we only report the energies from the MCTDH computations. C_{2v} symmetry operators are implemented which directly yield the characters of the vibrational wave functions. (see Tab. 1 for C_{2v} / D_{3h} correlations.) Furthermore, the vibrational wave functions of the DVR calculations are transformed back to the oscillator basis which allows the assignment of each state in terms of the underlying normal modes. The tentative assignments from that analysis are also given in the tables. Note, however, that harmonic normal modes quickly loose their significance in strongly anharmonic systems like NO_3 and thus the assignment of vibrational states becomes progressively meaningless. Furthermore, the e' normal modes of the NO_3 ground state are far from the typical asymmetric stretch and bend coordinates as found for the NO_3^- anion. This was already observed by Stanton[57] and means that particularly for the higher ν_4 excitations the assignment of quantum numbers becomes fairly pointless. Eigenstates which cannot be assigned to a clear excitation in terms of normal modes are labeled by $(*)$ in the tables. The new dipole surface for the $\tilde{X}$ state was used to compute the dipole transition probabilities for IR transitions also presented in the tables. These calculations were performed using the DVR method in which it is trivial to evaluate the integrals needed in the evaluation of

$$P_{f\leftarrow 0} = |\langle \Psi_f | \vec{\mu}(\boldsymbol{Q}) | \Psi_0 \rangle|^2 \cdot \delta(E_0 - E_f + h\nu). \tag{10}$$

The IR intensities are proportional to the corresponding transition probabilities.

We first discuss the results for the most abundant $^{14}N^{16}O_3$ isotopologues. The first seven computed eigenstates are in agreement with all experimental and previous theoretical results. The lowest excited state is assigned to 4^1 and is computed at 361 cm^{-1} in excellent agreement with high-resolution IR results of 365.5 cm^{-1}.[26] This is by far the strongest of all computed IR transitions. There are two levels corresponding to 4^2 with symmetries a_1' and e' of which only the latter is IR allowed. The computed energy of 742 cm^{-1} for the e' state corresponds reasonably well with the experimental value of 771.8 cm^{-1}.[26] The a_1' level also has been detected at 751.8 cm^{-1} and is computed at 711 cm^{-1} in our simulation.[26] The next computed level is found at 748 cm^{-1} for 2^1 in good agreement with the experimental value at 762.3 cm^{-1}.[26] The state computed at 1021.8 cm^{-1} can be assigned clearly to the 3^1 fundamental which has been the subject of a long lasting dispute. Our result is in agreement, though found at slightly lower energy, with previous high-level theoretical treatments[34, 57, 59, 60] and more recent experimental assignments.[32, 28, 118] We note that the computed IR intensity is the second highest of all states considered here. Nevertheless, it seems that this state was not observed by high-resolution IR spectroscopy. The reason for this is unknown (see discussion below). An experimental value around 1060 cm^{-1} has been detected by laser induced fluorescence but has been assigned to the ν_1 fundamental[19, 30]. This is in agreement with the level we compute at 1038.6 cm^{-1}. However, this 1^1 transition is of a_1' symmetry and thus IR inactive as can be seen from our intensity calculations. The ν_1 fundamental is followed by the three levels corresponding to 4^3 between 1082 and 1140 cm^{-1} of which only the e' level is IR active though absorbing much weaker than the previously

Table 3: Vibrational term values of $^{14}N^{16}O_3$, excitation energies in cm^{-1} with respect to zero-point level (2383.33 cm^{-1}), level symmetries in C_{2v} and D_{3h}, state assignments, and IR intensities (arbitrary units).

state	$E_i - E_0$	$\Gamma_{C_{2v}}$	$\Gamma_{D_{3h}}$	assignment	IR intensity
1	0.0	a_1	$a_1^{'}$	0	
2/3	361.1	b_1/a_1	$e^{'}$	4^1	0.778×10^{-02}
4	711.0	a_1	$a_1^{'}$	4^2	
5/6	742.2	b_1/a_1	$e^{'}$	4^2	0.448×10^{-03}
7	748.5	b_2	$a_2^{''}$	2^1	0.860×10^{-03}
8/9	1021.8	a_1/b_1	$e^{'}$	3^1	0.135×10^{-02}
10	1038.6	a_1	$a_1^{'}$	1^1	
11/12	1082.5	b_1/a_1	$e^{'}$	4^3	0.173×10^{-04}
13/14	1109.6	a_2/b_2	$e^{''}$	2^14^1	
15	1134.6	b_1	$a_2^{'}$	4^3	
16	1139.7	a_1	$a_1^{'}$	4^3	
17	1302.4	b_1	$a_2^{'}$	3^14^1	
18/19	1388.1	a_1/b_1	$e^{'}$	1^14^1	0.280×10^{-03}
20	1425.0	a_1	$a_1^{'}$	$(*)$	
21/22	1438.6	a_1/b_1	$e^{'}$	3^14^1	0.939×10^{-03}
23	1446.9	a_1	$a_1^{'}$	$4^4/4^5$	
24	1459.2	b_2	$a_2^{''}$	2^14^2	0.209×10^{-07}
25/26	1469.1	b_1/a_1	$e^{'}$	4^4	0.381×10^{-04}
27/28	1490.2	a_2/b_2	$e^{''}$	2^14^2	
29	1496.2	a_1	$a_1^{'}$	2^2	
30/31	1542.0	a_1/b_1	$e^{'}$	4^4	0.249×10^{-05}
32/33	1678.2	a_1/b_1	$e^{'}$	3^14^2	0.369×10^{-03}
34	1736.4	a_1	$a_1^{'}$	1^14^2	
35/36	1763.1	b_2/a_2	$e^{''}$	2^13^1	
37/38	1772.6	b_1/a_1	$e^{'}$	1^14^2	0.760×10^{-04}
39	1783.5	b_2	$a_2^{''}$	1^12^1	0.240×10^{-05}
40	1803.9	b_1	$a_2^{'}$	$3^14^2/3^14^3$	
41/42	1810.7	a_1/b_1	$e^{'}$	$(*)$	0.187×10^{-04}
43/44	1830.1	a_2/b_2	$e^{''}$	2^14^3	
45/46	1831.2	a_1/b_1	$e^{'}$	$(*)$	0.916×10^{-05}
47/48	1857.3	b_1/a_1	$e^{'}$	2^24^1	0.458×10^{-06}
49	1860.4	b_1	$a_2^{'}$	$(*)$	
50	1861.3	a_1	$a_1^{'}$	$(*)$	
51	1881.7	a_1	$a_1^{'}$	$(*)$	
52	1882.0	a_2	$a_1^{''}$	2^14^3	
53	1887.0	b_2	$a_2^{''}$	2^14^3	0.212×10^{-07}
54	1914.2	a_1	$a_1^{'}$	$(*)$	

discussed transitions. The next state with considerable oscillator strength is assigned to 1^14^1 at 1388 cm^{-1} which is in reasonable agreement with an LIF feature assigned to this state at 1420 cm^{-1}.[30] The second state strongly debated corresponds to 3^14^1 (e') and is calculated at 1439 cm^{-1} compared to an experimental

Table 4: Vibrational term values of $^{15}NO_3$, excitation energies in cm^{-1} with respect to zero-point (2352.13 cm^{-1}), level symmetries in C_{2v} and D_{3h}, state assignments including dominant state contributions, and IR intensities (arbitrary units).

state	E_0 or $E_i - E_0$	$\Gamma_{C_{2v}}$	$\Gamma_{D_{3h}}$	assignment	IR intensity
1	0.0	a_1	$a_1^{'}$	0	
2/3	356.3	b_1/a_1	$e^{'}$	4^1	0.772×10^{-02}
4	702.5	a_1	$a_1^{'}$	4^2	
5	729.2	b_2	$a_2^{''}$	2^1	0.837×10^{-03}
6/7	732.2	b_1/a_1	$e^{'}$	$(*)$	0.461×10^{-03}
8/9	1008.4	a_1/b_1	$e^{'}$	3^1	0.120×10^{-02}
10	1038.1	a_1	$a_1^{'}$	1^1	
11/12	1069.6	b_1/a_1	$e^{'}$	$(*)$	0.147×10^{-04}
13/14	1085.5	a_2/b_2	$e^{''}$	2^14^1	
15	1118.8	b_1	$a_2^{'}$	4^3 (?)	
16	1124.8	a_1	$a_1^{'}$	4^3 (?)	
17	1287.0	b_1	$a_2^{'}$	3^14^1	
18/19	1380.4	a_1/b_1	$e^{'}$	1^14^1	0.394×10^{-03}
20	1404.1	a_1	$a_1^{'}$	$(*)$	
21/22	1420.4	a_1/b_1	$e^{'}$	$(*)$	0.811×10^{-03}
23	1431.1	a_1	$a_1^{'}$	$(*)$	
24	1431.4	b_2	$a_2^{''}$	$(*)$	0.203×10^{-07}
25/26	1452.6	b_1/a_1	$e^{'}$	$(*)$	0.717×10^{-04}
27	1457.6	a_1	$a_1^{'}$	2^2	
28/29	1460.9	a_2/b_2	$e^{''}$	$(*)$	
30/31	1521.1	a_1/b_1	$e^{'}$	$(*)$	0.433×10^{-05}
32/33	1658.6	a_1/b_1	$e^{'}$	$(*)$	0.376×10^{-03}
34	1726.8	a_1	$a_1^{'}$	$(*)$	
35/36	1730.8	b_2/a_2	$e^{''}$	$(*)$	
37/38	1758.2	a_1/b_1	$e^{'}$	$(*)$	0.550×10^{-04}
39	1763.7	b_2	$a_2^{''}$	1^12^1	0.232×10^{-05}
40	1780.1	b_1	$a_2^{'}$	$(*)$	
41/42	1784.9	a_1/b_1	$e^{'}$	$(*)$	0.273×10^{-04}
43/44	1798.1	a_2/b_2	$e^{''}$	$(*)$	
45/45	1811.0	a_1/b_1	$e^{'}$	$2^24^1(*)$	0.446×10^{-05}
47/48	1815.1	a_1/b_1	$e^{'}$	$2^24^1(*)$	0.691×10^{-05}
49	1836.0	a_1	$a_1^{'}$	$(*)$	
50	1838.6	b_1	$a_2^{'}$	$(*)$	
51	1846.9	a_2	$a_1^{''}$	$(*)$	
52	1852.9	b_2	$a_2^{''}$	$(*)$	0.382×10^{-07}

band at 1492 cm^{-1}. We compute the third strongest IR intensity for this transition and cannot find any other strong transition in that energy region. Thus, our result clearly supports the assignment of the 1492 cm^{-1} feature to the 3^14^1 (e') transition. The 3^14^1 configuration gives rise to three sub-levels of e', a_1', and a_2' symmetry. The a_2' level corresponding to 3^14^1 is found at much lower energy at 1302 cm^{-1} which is rather unexpected and might indicate some remaining problems with the PES model. The a_1' level

Table 5: Vibrational term values of $^{14}N^{18}O$ $^{16}O_2$, excitation energies in cm^{-1} with respect to zero-point level (2355.5 cm^{-1}), level symmetries in C_{2v}, state assignments including dominant state contributions, and IR intensities (arbitrary units).

state	$E_i - E_0$	$\Gamma_{C_{2v}}$	assignment	IR intensity
1	0.0	a_1	0	
2,3	354.0, 358.9	b_1, a_1	4^1_y, 4^1_x	0.383×10^{-02}, 0.383×10^{-02}
4	700.8	a_1	4^2_y	0.582×10^{-05}
5,6	732.4, 733.8	b_1, a_1	$4^1_x4^1_y$, 4^2_x	0.207×10^{-03}, 0.207×10^{-03}
7	745.4	b_2	2^1	0.858×10^{-03}
8,9	993.9, 1017.9	a_1, b_1	3^1_x, 3^1_y	0.474×10^{-03}, 0.738×10^{-03}
10	1030.5	a_1	1^1	0.216×10^{-03}
11,12	1062.5, 1072.7	b_1, a_1	4^3_y, 4^3_x	0.825×10^{-05}, 0.905×10^{-05}
13,14	1099.5, 1104.2	a_2, b_2	$2^14^1_y$, $2^14^1_x$	– , 0.104×10^{-08}
15	1120.5	b_1	$4^2_x4^1_y$	0.427×10^{-07}
16	1125.2	a_1	$4^1_x4^2_y$	0.539×10^{-06}
17	1285.4	b_1	$3^1_x4^1_y/3^1_y4^1_x$	0.560×10^{-05}
18, 19	1358.6, 1372.0	b_1, a_1	$1^14^1_y$, $1^14^1_x$	0.144×10^{-03}, 0.350×10^{-04}
20	1407.8	a_1	$3^1_x4^1_x$	0.265×10^{-03}
21	1418.0	a_1	$3^1_y4^1_y$	0.245×10^{-03}
22	1425.9	a_1	$(*)$	0.539×10^{-04}
23	1430.1	b_1	$(*)$	0.411×10^{-03}
24	1446.0	b_2	$2^14^2_y/2^14^2_x$	0.195×10^{-07}
25,26	1449.2, 1451.5	b_1, a_1	$(*)$, $(*)$	0.321×10^{-04}, 0.371×10^{-05}
27,28	1477.3, 1478.7	a_2, b_2	$2^14^1_x4^1_y$, $2^14^2_x$	– , 0.361×10^{-09}
29	1490.1	a_1	2^2	0.214×10^{-06}
30,31	1522.1, 1522.9	b_1, a_1	$4^3_x4^1_y/4^1_x4^3_y$, $4^2_x4^2_y$	0.158×10^{-06}, 0.641×10^{-06}
32,33	1646.8, 1666.4	a_1, b_1	$3^1_x4^2_y$, $3^1_y4^2_x$	0.166×10^{-03}, 0.180×10^{-03}
34	1709.5	a_1	$1^14^2_y/1^14^2_x$	0.725×10^{-05}
35,37	1733.7, 1754.9	b_2, a_2	$2^13^1_x/1^12^1$, $2^13^1_y$	0.590×10^{-06}, –
36,38	1736.2, 1755.9	b_1, a_1	$1^14^1_x4^1_y$, $1^14^2_x/1^14^2_y$	0.231×10^{-04}, 0.556×10^{-04}
39	1771.2	b_2	1^12^1	0.176×10^{-05}
40	1783.5	b_1	$3^1_x4^3_y$	0.187×10^{-07}
41,42	1786.8, 1790.3	b_1, a_1	$(*)$, $(*)$	0.355×10^{-05}, 0.335×10^{-05}
43,46	1807.3, 1817.2	a_2, b_2	$2^14^3_y$, $2^14^3_x$ $(*)$	– , 0.213×10^{-08}
44,45	1807.9, 1808.0	a_1, b_1	$(*)$, $(*)$	0.183×10^{-05}, 0.156×10^{-04}
47	1836.0	b_1	$(*)$	0.113×10^{-06}
48	1839.7	a_1	$(*)$	0.663×10^{-07}
49,50	1844.3, 1848.6	b_1, a_1	$2^24^1_y$, $2^24^1_x$	0.296×10^{-06}, 0.349×10^{-06}
51	1856.1	a_1	$(*)$	0.366×10^{-05}
52	1864.9	a_2	$2^14^2_x4^1_y$	–
53	1869.4	b_2	$2^14^1_x4^2_y$ $(*)$	0.151×10^{-07}

cannot be clearly assigned to any of the states analysed here. Possible candidates in reasonable energetic proximity would be the levels computed at 1425.0 or 1446.9 cm^{-1}. The decomposition of the computed level at 1425 $cm^{-1}$of a'_1 symmetry into the harmonic oscillator basis shows a strong mixing of excitations in terms of normal modes, which does not allow for a clear assignment. It does contain some contributions of 3^14^1

Table 6: Summary of the comparison between experimental and computed transition energies for NO_3 (in cm^{-1}). Experimental data as summarized in ref. [118]. See text for discussion.

assignment	E_{exp}	E_{theo}	IR	$E_{exp} - E_{theo}$	$^{15}\Delta_{exp}$	$^{15}\Delta_{theo}$
$4^1\ e'$	365.5	361.1	0.778×10^{-02}	4.4	-5.3	-4.8
$4^2\ a_1'$	752.4	711.0		41.4	-9.8	-8.5
$4^2\ e'$	771.8	742.2	0.448×10^{-03}	29.6	-10.6	-10.0
$2^1\ a_2''$	762.3	748.5	0.860×10^{-03}	13.8	-19.6	-19.3
$1^1\ a_1'$	1051.2	1038.6		12.6	1.5	-0.5
$3^1\ e'$	1055.3	1021.8	0.135×10^{-02}	33.5	-16.7	-13.4
$2^1 4^1\ e''$	1125.1	1109.6		15.5	-25.1	-24.1
$4^3\ e'$	1173.6	1082.5	0.173×10^{-04}	91.1	-14.4	-12.9
$4^3\ a_1'$	1214	1139.7		74.3	-15.0	-14.9
$1^1 4^1\ e'$	1413.6	1388.1	0.280×10^{-03}	25.5	-6.5	-7.7
$3^1 4^1\ a_2'$	1491	1302.4 (?)		188.6 (?)	-26.0	-15.4
$3^1 4^1\ e'$	1492.4	1438.6	0.939×10^{-03}	53.8	-19.6	-18.2
$3^1 4^1\ a_1'$	1499.8	-		-	-24.6	
$2^1 4^2\ a_2''$	1509.7	1459.2	0.209×10^{-07}	50.5	-29.6	-27.8
$2^2\ a_1'$	1522	1496.2		25.8	-39.0	-38.6
$2^1 4^2\ e''$	1537.5	1490.2		47.3	-5.5	-29.3
$1^1 4^2\ a_1'$	1773.8	1736.4		37.4	-10.0	-9.6
$1^1 4^2\ e'$	1793	1772.6	0.760×10^{-04}	20.4	-10.0	-14.4
$1^1 2^1\ a_2''$	1810	1783.5	0.240×10^{-05}	26.5	-20.0	-19.8
$2^1 3^1\ e''$	1815	1763.1		51.9	-40.0	-32.3
$2^2 4^1\ e'$	1885	1857.3	0.458×10^{-06}	27.7	-45.0	-42.2
$2^1 4^3\ e''$	1929.4	1830.1		99.3	-33.6	-32.0
$2^1 4^3\ a_1''$	1937.7	1882.0		55.7	-30.4	-35.1
$2^1 4^3\ a_2''$	1970	1887.7	0.212×10^{-07}	82.3	-34.0	-34.1

Table 7: Contributions of diabatic electronic states to low energy vibronic eigenstates.

Energy	$\tilde{X}\ ^2A_2'$	$\tilde{A}\ ^2E_x''$	$\tilde{A}\ ^2E_y''$	$\tilde{B}\ ^2E_x'$	$\tilde{B}\ ^2E_y'$
0.0	0.976	0.3×10^{-9}	0.3×10^{-9}	0.12×10^{-1}	0.12×10^{-1}
361.1	0.966	0.3×10^{-9}	0.3×10^{-9}	0.17×10^{-1}	0.17×10^{-1}
361.1	0.966	0.3×10^{-9}	0.3×10^{-9}	0.17×10^{-1}	0.17×10^{-1}
711.0	0.958	0.3×10^{-9}	0.3×10^{-9}	0.21×10^{-1}	0.21×10^{-1}
742.2	0.958	0.4×10^{-9}	0.4×10^{-9}	0.21×10^{-1}	0.21×10^{-1}
742.2	0.958	0.4×10^{-9}	0.4×10^{-9}	0.21×10^{-1}	0.21×10^{-1}
748.5	0.977	0.8×10^{-9}	0.8×10^{-9}	0.12×10^{-1}	0.12×10^{-1}
1021.8	0.957	0.1×10^{-8}	0.1×10^{-8}	0.21×10^{-1}	0.21×10^{-1}
1021.8	0.957	0.1×10^{-8}	0.1×10^{-8}	0.21×10^{-1}	0.21×10^{-1}
1038.6	0.972	0.4×10^{-9}	0.4×10^{-9}	0.14×10^{-1}	0.14×10^{-1}
1082.5	0.952	0.3×10^{-9}	0.3×10^{-9}	0.24×10^{-1}	0.24×10^{-1}
1082.5	0.952	0.3×10^{-9}	0.3×10^{-9}	0.24×10^{-1}	0.24×10^{-1}
1109.6	0.966	0.1×10^{-8}	0.9×10^{-9}	0.21×10^{-1}	0.13×10^{-1}
1109.6	0.966	0.9×10^{-9}	0.1×10^{-8}	0.13×10^{-1}	0.21×10^{-1}
1134.6	0.953	0.4×10^{-9}	0.4×10^{-9}	0.23×10^{-1}	0.23×10^{-1}
1139.7	0.951	0.4×10^{-9}	0.4×10^{-9}	0.25×10^{-1}	0.25×10^{-1}
1302.4	0.945	0.1×10^{-8}	0.1×10^{-8}	0.27×10^{-1}	0.27×10^{-1}
1388.1	0.959	0.6×10^{-9}	0.6×10^{-9}	0.20×10^{-1}	0.21×10^{-1}
1388.1	0.959	0.6×10^{-9}	0.6×10^{-9}	0.21×10^{-1}	0.20×10^{-1}
1425.0	0.948	0.2×10^{-8}	0.2×10^{-8}	0.26×10^{-1}	0.26×10^{-1}

configurations, though. Comparison with the experimental assignment[27] would make the next level about 8 cm^{-1} above at 1446.9 cm^{-1} a likely candidate but this state is mostly composed of 4^4 and 4^5 configurations in disagreement with the interpretation of the experimental data. Tab. 6 gathers the comparisons discussed above between experimental frequencies as summarized in ref. [118] and our theoretical results.

The level energies for the higher states are in less good agreement with experimental assignments and the analysis in terms of normal modes is getting progressively more uncertain. It is also worth noting that the different high-level *ab initio* quantum dynamics calculations of the vibrational level energies (and assignments) all deviate considerably, even among studies by the same authors.[34, 57, 59, 60] One possible reason could be the treatment of the vibronic coupling to the $\tilde{B}$ state, which is also invoked for the explanation of various perturbations observed in the high-resolution spectra. We therefore tested the role of the $\tilde{B}$ state by a number of calculations. First of all, we computed the contributions of the five diabatic electronic states to the lowest 20 eigenstates (Tab. 7). We computed the eigenstates using both the adiabatic as well as the diabatic electronic basis and found basically no difference in the level energies. The diabatic contributions are obtained directly from the normalized DVR state eigenvectors of the diabatic calculation as norms of the five sub-vectors each belonging to one of the five diabatic electronic states. As is not surprising, all states are by far dominated by the $\tilde{X}$ state contribution and the $\tilde{A}$ state has a negligible effect. The $\tilde{B}$ state contributes between 2–5 % to the total state composition with a very slight tendency to mix in increasingly

with higher vibrational level energy as would be expected. These results can be used also to test arguments in the debate about the assignment of the experimental 1492 cm^{-1} band. In the debate between the groups of Hirota[119] and Kawaguchi[28] the vibronic coupling between the $\tilde{X}$ and $\tilde{B}$ state plays a key role. One argument concerns the observed effective spin-orbit (SO) coupling in the non-degenerate $^2A_2'$ ground state that can only originate from a contribution by a degenerate excited electronic state. We computed the SO splittings of the excited states at MRCI level of theory and found values of -1 cm^{-1} for the $\tilde{A}$ $^2E''$ state and -107 cm^{-1} for the $\tilde{B}$ $^2E'$ state, respectively. The latter is in excellent agreement with the experimental estimate of -105 cm^{-1} by Tada *et al.*[120] The value of -105 cm^{-1} corresponds to an effective SO coupling constant of -21 cm^{-1} and a contribution of 5 % $\tilde{B}$ state to the $\tilde{X}$ state vibronic levels would correspond to an effective SO coupling constant of -1.05 cm^{-1} for $\tilde{X}$ state levels in stark contrast to the experimental value of -0.167 cm^{-1}.

The coupling between the $\tilde{X}$ and the $\tilde{B}$ state has also been invoked to explain anomalies in line intensities in both IR spectra and the photodetachment spectrum of the NO_3^- anion.[27, 59] Stanton computed the IR absorption intensity for the 3^1 fundamental to be very low despite it being an allowed e' level and the asymmetric stretching mode inducing a significant change in dipole moment.[57] This result cannot be reproduced by our current model for the PES and the dipole surface. The pronounced non-linearity and multi-mode dependence of the dipole surface that we observe may indicate the influence of the vibronic $\tilde{X}$-$\tilde{B}$ coupling. However, this dipole surface results in a considerable IR intensity for the ν_3 fundamental in contrast to experimental observations. Kawaguchi *et al.* suggested that the sizable coupling to the $\tilde{B}$ state together with the large $\tilde{X}$-$\tilde{B}$ transition moment leads to intensity cancellation for the 3^1 transition.[27] This seems a reasonable explanation. The numerical test of this hypothesis is beyond the scope of the present study but will be investigated in the near future.

The vibrational eigenstates for the $\tilde{X}$ state have been calculated as well for two isotopologues, namely $^{15}N^{16}O_3$ and $^{14}N^{18}O^{16}O_2$, and the corresponding results are summarized in Tabs. 4 and 5, respectively. For $^{15}N^{16}O_3$, the system remains D_{3h} symmetric and thus the vibrational states have the same symmetry labels as for the natural isotopologues. By contrast, $^{14}N^{18}O^{16}O_2$ only has C_{2v} symmetry and thus all levels corresponding to e' and e'' symmetry for $^{14}N^{16}O_3$ and $^{15}N^{16}O_3$ will split into a_1/b_1 and a_2/b_2 levels, respectively. Experimental values are available for the isotopic shifts of some of the vibrational levels. Beckers *et al.* studied isotopic shifts of $^{15}N^{16}O_3$ in a Ne matrix at 4.3 K and for the first time observed the shifts for the 4^1 state of -5.3 cm^{-1}, the 3^1 state of -12.8 cm^{-1}, and the 1^14^1 state of -6.6 cm^{-1}.[33] The corresponding computed values are -4.8 cm^{-1}, -13.4 cm^{-1}, and -7.7 cm^{-1}, respectively, in very good agreement with experiment (c. f. Tab. 6). Fujimori *et al.* studied the same isotopologue and thoroughly investigated three states.[26] The 2^1 level shows an isotopic shift of -19.6 cm^{-1} in excellent agreement with our computed value of -19.3 cm^{-1}. For the two states corresponding to 4^2 excitation the experimental values are -9.2 cm^{-1} for the a_1' level and -10.5 cm^{-1} for the e' state. Our corresponding computed values are

-8.5 cm^{-1} and -10.0 cm^{-1}, both in excellent agreement with experiment. The isotopic shifts of three other levels have been determined experimentally by Kawaguchi *et al.*, most importantly the 1492 cm^{-1} feature under debate.[27] They observed a shift of -19.6 cm^{-1} for the e' state corresponding to $3^1 4^1$ excitation in nearly perfect agreement with our computation of -19.3 cm^{-1}. By contrast, they assign a feature at 1499 cm^{-1} to the a_1' state for the same excitation with an isotopic shift of -24.6 cm^{-1} which is not found in our simulations. We find a state 8 cm^{-1} above the $3^1 4^1$ e' state at 1447 cm^{-1} but its isotopic shift is only -15.6 cm^{-1}. We also compute a 2^2 a_1' state at 1497 cm^{-1} with a shift of -38.6 cm^{-1} which can be ruled out as well. Another candidate with a_1' symmetry cannot be clearly assigned from our calculations and is computed at 1425 cm^{-1} with a shift of -20.9 cm^{-1}. This represents the closest match in the isotopic shift though the computed level energies is in less good agreement with experiment.

Finally, Kawaguchi *et al.* assigned a feature at 1557.3 cm^{-1} to the $2^1 4^2$ e'' state and determined an isotopic shift of -5.5 cm^{-1}. The present PES model yields a calculated transition at 1490.2 cm^{-1} with a corresponding shift of -29.6 cm^{-1} for the same state. The computed isotopic shifts of all undisputed states are all within 2 cm^{-1} of the experimental values. Therefore, we can use the isotopic shifts as indicator for inconsistencies in the assignments between theory and experiment. Kawaguchi *et al.* recently presented a summary of level energies, assignments, and isotopic shift, which we use in Table 6 to compare to the data obtained in the present work. We notice that particularly two levels show stark discrepancies between our results and Kawaguchi's assignments, namely the $3^1 4^1$ (a_2') level and the $2^1 4^2$ (e'') state. In the first case our result for the shift is lower than the sum of the single mode shifts while the opposite is true for the experimental assignment. For the above mentioned e'' state the experimental result seems rather inconsistent with the single mode shifts while the theoretical result seems to match perfectly. Therefore, a re-investigation of these particular bands might be worthwhile. We also note that of all the fundamentals the ν_3 one shows the largest deviation between experimental and theoretical isotope shift. The reason for this is unknown but the result indicates a different nuclear motion predicted by theory compared to experiment. Together with the observation that the ν_4 progression seems to have the wrong anharmonicity behaviour compared to experiment, rendering level energies involving higher ν_4 excitations progressively less accurate, this might indicate some remaining deficiency of the PES model. This will be addressed in forthcoming work.

The results of the simulation of the $^{14}N^{18}O^{16}O_2$ isotopologue are also presented in Tab. 5. Unfortunately, experimental measurements are limited to only two Ne matrix studies [32, 33] in which the 4^1 fundamental was observed as two transitions at 361.1 and 357.9 cm^{-1} in excellent agreement with our theoretical results of 359.0 and 354.0 cm^{-1}, respectively. Two isotopic shifts of -25.4 and -9.8 cm^{-1} were observed for the split $3^1 4^1$ (e') levels. From the wave function analysis we find two states (levels 20 and 21 in Tab. 5) clearly correlating to this transition with computed isotope shifts of -30.2 and -20.1 cm^{-1}, respectively. Both levels correspond to a_1 symmetry and show shifts in reasonable though not great agreement with one of the shifts

determined experimentally. It is clear that only one of the two states can correlate to the $3^1 4^1$ (e') transition in $^{14}N^{16}O_3$. The only b_1 state computed nearby should be the other component and its isotopic shift of -8.8 cm^{-1} would be in rather good agreement with the experimental value. These isotopic shift together with the shifts obtained for $^{15}N^{16}O_3$ yield additional support for the assignment of the prominent 1492 cm^{-1} feature to the $3^1 4^1$ combination band. The remaining results cannot be compared to experimental results and thus may serve as a prediction for possible future experimental investigations.

5. Conclusions

In the present work a new full-dimensional diabatic PES model for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ state of the NO_3 radical is presented and the vibrational dynamics of the $\tilde{X}$ state is investigated using this model. The new PES model accurately represents a large number (roughly 90 000 energies) of high-level MRCI *ab initio* data, though still leaving room for improvement. Using the same technology, an accurate adiabatic dipole surface for the $\tilde{X}$ state was determined also. The new model is used in the present study to compute the IR spectrum of NO_3 up to approximately 2000 cm^{-1}. In addition, isotopic shifts are determined for the two species $^{15}N^{16}O_3$ and $^{14}N^{18}O^{16}O_2$, which yields important additional data to settle a long lasting debate about the assignment of a prominent spectral feature observed experimentally at 1492 cm^{-1}.

Vibrational frequencies are computed in good to excellent agreement with experimental values for most of the computed and measured levels. The observed errors are smaller for the fundamentals than for most of the combination bands and the largest error is observed for the disputed level at 1492 cm^{-1} for which the present calculations yield 1438 cm^{-1}. Since the analytical representation of the PES data is very accurate with rms errors of only 100 cm^{-1} up to 1 eV above minimum, the deficiencies in the PES are most likely due to the electronic structure calculations. However, effects of the data point sampling cannot be ruled out and will be investigated in forthcoming work. All computed frequencies are lower than the experimental values indicating that the MRCI method slightly underestimates the binding strength in NO_3. This might be due to the very complicated electronic structure in which the mixing to the Jahn-Teller active $\tilde{B}$ state plays a significant role, which also leads to complications in the nuclear dynamics.

The computed vibrational eigenstates are also analysed in terms of the harmonic oscillator basis and diabatic electronic states. It is found that the $\tilde{B}$ state contributes between 2–5 % to the vibrational states associated with the $\tilde{X}$ state while the contributions of the $\tilde{A}$ state are negligible. The analysis of the eigenstates in terms of vibrational quanta is possible for most transitions of lower energy though the significant anharmonicity and strong mode mixing present in NO_3 renders this progressively meaningless for higher transitions. Nevertheless, most assignments based on the present calculations are in agreement with experimental analyses from high-resolution IR spectra. This is particularly important for the assignment of the debated 1492 cm^{-1} feature. According to our calculations this is clearly a $3^1 4^1$ combination band in agreement with previous high-level theoretical studies. The ν_3 fundamental is predicted around 1022 cm^{-1},

also in agreement with all other theoretical results. The evidence for this assignment is further strengthened by the computed isotopic shifts for the $^{15}N^{16}O_3$ isotopologue. For all levels for which the assignments are undisputed the computed and experimentally determined isotope shifts are within 2 cm^{-1}, usually much better. This is also true for the $3^1 4^1$ transition which has a significantly larger isotope shift than the 3^1 transition. If the 1492 cm^{-1} feature was assigned to the ν_3 fundamental, the isotope shift would be clearly inconsistent with the theoretical prediction. One striking disagreement we find between the present calculations and experimental observations of the IR intensities. The present calculations using an accurate representation of the adiabatic dipole surfaces for the $\tilde{X}$ state predict a fairly strong absorption for the 3^1 transition but this feature is at most very weak in experimental IR spectra. It is likely that the absorption intensities are influenced by vibronic coupling to the $\tilde{B}$ state and a much more elaborate diabatic model for the dipole operator would be needed to account for these effects. This will be subject to future work because it is beyond the scope of the present study.

The present results show that the developed diabatic PES model yields very good results for the $\tilde{X}$ state and thus similarly accurate results can be expected for the nuclear dynamics in the excited states. The results also give further support for the assignment of the 1492 cm^{-1} feature to a $3^1 4^1$ combination band rather than the ν_3 fundamental, which is expected around 1022 cm^{-1}. This work will be continued by further improvements of the diabatic PES model which will be used for forthcoming quantum dynamics studies of this interesting but challenging molecular system.

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