

Submillimeter measurements of isotopes of nitric acid

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Abstract

The ground and low-lying vibrational states of nitric acid are observable with current instrumentation in the Earth's thermal submillimeter atmospheric emission. Remote sensing continues to improve to higher sensitivity and future missions will allow these measurements with minimal integration time. Sensing of weaker spectral features will require signal averaging, and choices of spectral windows for these features will require knowledge of the higher vibrational states and rare isotopes of the strongly emitting species. Nearly comprehensive information on vibrational states and isotopically substituted species is now available from wide bandwidth scans of natural and isotopically enriched nitric acid. In this work, ground state rotational spectra of five isotopically substituted species of nitric acid are analyzed in the submillimeter spectral range. We present the Hamiltonian parameters necessary for prediction and identification of isotopic features across the nitric acid ground state rotational spectrum.

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1. Introduction

Remote sensing and in-situ measurements of the Earth's atmosphere continue to progress to higher sensitivities that enable weaker absorptions to be detected. The drive to measure new and interesting chemical species will be limited not only by the technology, but also by the congestion of the spectrum. The nitric acid rotational spectrum has been an easy target for thermal emission remote sensing [1] because of its strong features due to a large dipole moment. However, due to its polyatomic, heavy-atom framework, there are also a number of satellite features due to thermal vibrational excitation and natural isotopic enrichment. The large number of features in the thermal

emission spectrum presents a confusion limitation for the detection of other trace species with smaller abundance, weaker dipole moment, or both. Future missions planning to observe new species require a reliable listing of known transitions to screen for features that would be visible upon deep integration with a sensitive receiver.

The stable species nitric acid, HONO₂, is an atmospheric sink for the ozone destroying HO_x and NO_x cycles. The HONO₂ volume mixing ratio typically peaks from 5 to 15 ppb at altitudes between 20 and 30 km, where it interacts with ozone chemistry. Utilizing millimeter or submillimeter radiometry, the species is now continuously globally monitored through its thermal emission [1]. In addition to the 'routine' nitric acid chemistry, continuous monitoring has revealed more extreme events, both periodic and aperiodic, that enhance our understanding of the atmosphere. For example, enhanced nitric acid was present under

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aerosol loaded conditions following the eruption of Mt. Pinatubo and denitrified air is characteristic of the annual south polar vortex chemical processing [2].

A continuing effort at one of our laboratories (OSU) has extended knowledge of the ro-vibrational ladder in this molecule [3–5], which has been furthered through simultaneous analysis of infrared spectra [6,7]. The current state of the art includes complete rotational analyses of the all states up to $\sim 1200\text{ cm}^{-1}$. At this excitation energy, the thermal populations ($\sim e^{-E_{\text{vib}}/kT}$) of individual vibrational states of the parent species are of the same order of magnitude as the natural abundances of the rare isotopes ^{15}N and ^{18}O , and the presence of these satellite spectra become just as important as the vibrational contributions.

Just over 1% of nitric acid molecules contain at least one rare isotope. Based on IUPAC abundances [8], the main isotopomer mole fraction is 0.989088. Singly substituted isotopomers and isotopologues are listed in Table 1. In natural abundance the ^{15}N substituted isotopomer is equal in abundance to the thermal population (at 300 K) of a state with energy 1169 cm^{-1} , and therefore was essential to quantify and assign during the analysis of the three vibrational states of the parent species in this energy range. The equivalent energies for each of the single rare isotope species are also given in Table 1 to indicate at which analysis levels the different species should be incorporated. The previously available literature data was insufficient to accurately identify much of the rare isotope nitric acid spectra in the millimeter and submillimeter wavelengths. However, transitions of naturally abundant isotopomers and isotopologues are readily measurable. Furthermore, the nitric acid molecule is readily isotopically enriched, therefore it is sensible to perform experiments that unambiguously reveal the isotopic signatures, rather than trying to extract all of the features from within the congested thermal manifold of the parent species.

Nitric acid isotopomers have been studied with high resolution spectroscopy in the infrared ($\text{HO}^{15}\text{NO}_2$ [9], DONO_2 [10–13]), submillimeter wavelengths (DONO_2 [14]) and centimeter wavelengths [15–18]. The centimeter-wavelength studies were aimed at structural determination and, when combined with infrared data, both the equilibrium structure and a detailed force-field for the molecule were attained [17,18]. No studies have reported spectra for the ^{17}O substituted isotopologues, presumably due to the expense of raw material as well as the minimal gain in structural knowledge past ^{18}O substitution. The present study reports a systematic analysis of singly-substituted (^{15}N , ^{18}O , and ^2H) nitric acid ground state spectra in the millimeter and submillimeter spectral region.

2. Experimental details, results, and analysis

A series of multiplier chains, commercial, JPL built, and hybrid, were utilized to record spectra at JPL [19]. New measurements were performed for all isotopic species between 390 and 655 GHz and additional measurements of $\text{HO}^{15}\text{NO}_2$ and DONO_2 between 72–120 and 800–850 GHz were also performed. A section of ^{18}O enriched HONO_2 data recorded with the JPL system is given in Fig. 1. Spectra taken at OSU were measured with a synthesizer in the range 78–118 GHz and with the FASSST system [20] in the frequency range of 125–520 GHz for the parent and $\text{HO}^{15}\text{NO}_2$ isotopomer. A section of the FASSST spectrum of normal HONO_2 is shown in Fig. 2. Additionally, centimeter-wavelength spectra published in the literature were utilized from [15–17] and submillimeter spectra from [14]. Table 2 outlines the current data set used in each analysis.

Nitric acid enriched with ^{15}N was purchased from CDN isotopes and used directly in a slow flow or static system. Nitric acid enriched with ^{18}O was made inside the flow cell through reaction of ^{18}O enriched water (ICON isotopes) with the inorganic salt nitrosonium tetrafluoroboride (NOBF_4 , Aldrich). Deuterated nitric acid was obtained through simple mixture of deuterated water and concentrated nitric acid. In each enriched scan the wide band surveys indicated strong $^{\text{r}}$ -branch series for each isotopomer as well as numerous features due to the thermally populated vibrational levels of the isotopically enriched nitric acid. The current analysis has focused on the ground state features since the thermally populated isotopic states are still below the confusion limit in room temperature nitric acid spectra.

The data sets were each analyzed using a standard asymmetric top Watsonian with an A -type reduction in the I' representation. For each species this was a straightforward extension of previous data analyses. For the *cis*- ^{18}O isotopologue, new data entered into the analysis did not fit properly until the doublet $3_{0,3} \leftarrow 3_{1,2}$, $3_{1,3} \leftarrow 3_{1,2}$ transitions assigned to 30142.35 and 30141.12 MHz, respectively, in [16] were removed. After subsequent fitting the lower frequency feature could then be assigned to $3_{0,3} \leftarrow 3_{1,2}$ and the higher frequency transition to $3_{0_{25,5}} \leftarrow 3_{0_{25,6}}$. Similarly, the 30742.73 MHz $\text{H}^{18}\text{ONO}_2$ transition assigned by Cox and Riveros to $3_{0,3} \leftarrow 3_{2,2}$ did not fit well. Removing this value from the fit allowed the predicted transition frequency to move 1.6 MHz lower, very close to the *cis*- ^{18}O $6_{5,2} \leftarrow 6_{4,3}$ transition frequency which is approximately five times stronger.

Table 1
IUPAC [8] abundances for HNO_3 isotopomers and isotopologues

	$\text{HO}^{15}\text{NO}_2$	$^{18}\text{O HONO}_2$	$^{17}\text{O HONO}_2$	DONO_2
Mole fraction	0.003636	0.001987	0.000376	0.000154
Equivalent $E(\text{cm}^{-1})@300\text{ K}$	1169	1295	1642	1828

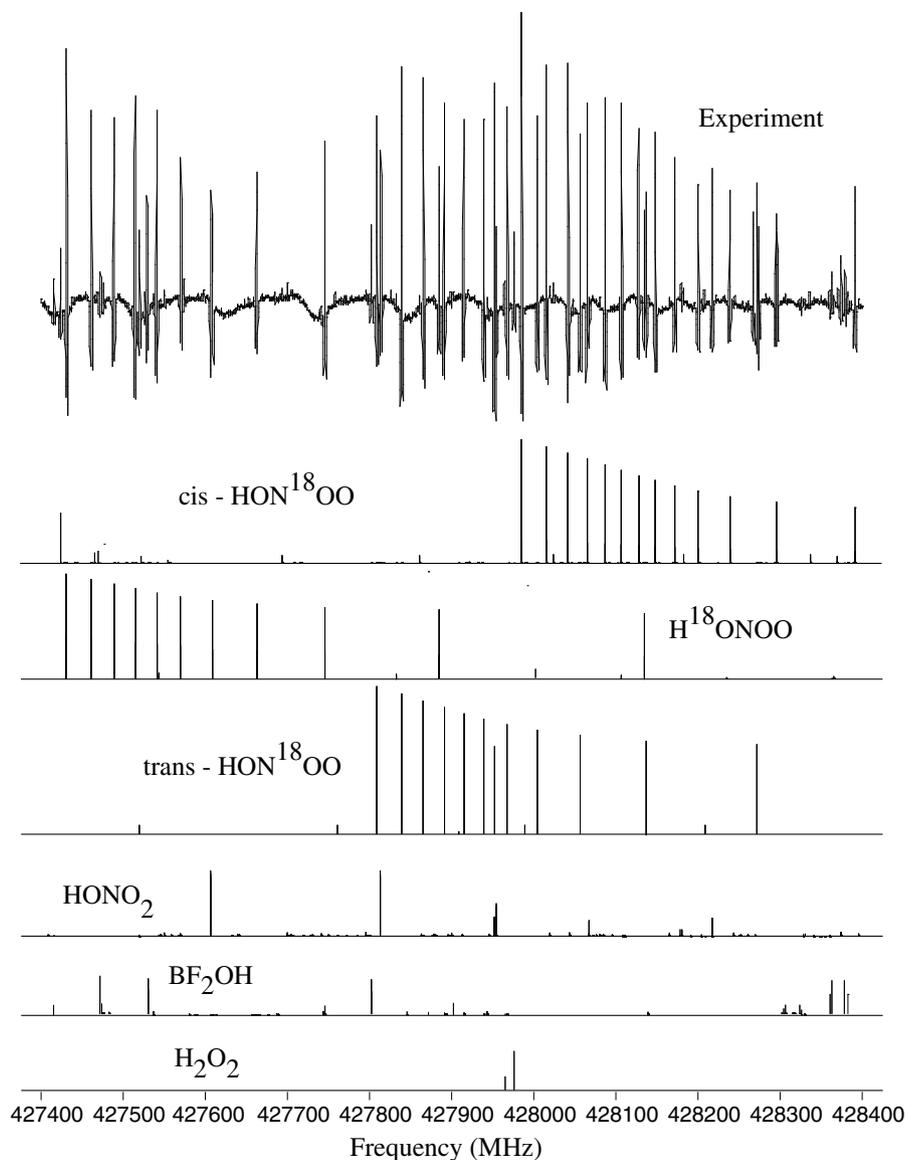


Fig. 1. Survey scan of ^{18}O enriched reactive system and identified transitions.

Parameters up to eighth order are determinable, with full sets of quartic and sextic parameters. The fitted parameters for each isotopic species are listed in Table 3. The 19 parameter set is sufficient for every species except $\text{HO}^{15}\text{NO}_2$, which requires one more octic term. Although some of the octic terms are not well determined, particularly for l_{JJK} or l_{KKJ} in the ^{18}O substituted species, the individual fits suffer from removal of these terms. To minimize error in the fitted parameters the data set was culled to include mainly non-blended features with consistent intensity values for the given assignment. The data are weighted appropriately to produce σ_{rms} values near unity for each spectral range or spectrometer. A σ_{rms} of unity indicates that the fitted parameter uncertainties (values in parenthesis after each parameter value in Table 3) are 1σ . Values of σ_{rms} less than unity indicate a conservative weighting and overestimation of statistical error. It is apparent from the well-determined quartic and sextic parameters that the

centrifugal distortion parameters differ significantly with isotopic substitution.

Results of the fits to the spectra have been deposited with the Journal and full listings of the necessary files, including predictions, are available in the JPL Spectral Line Catalog [21]. For prediction of the spectra it is important to use the dipole moment components appropriate for the axis system of the isotopomer. This allows relative strengths of the aR and bR branches to be reproduced well within the variance of power across the broad scan such as that shown in Fig. 1.

3. Discussion

The data set described in Table 2 and the results presented in Table 3 show a dramatic improvement in the accuracy of the fourth order and higher order parameters of the isotopic species. With the exception of DONO_2 ,

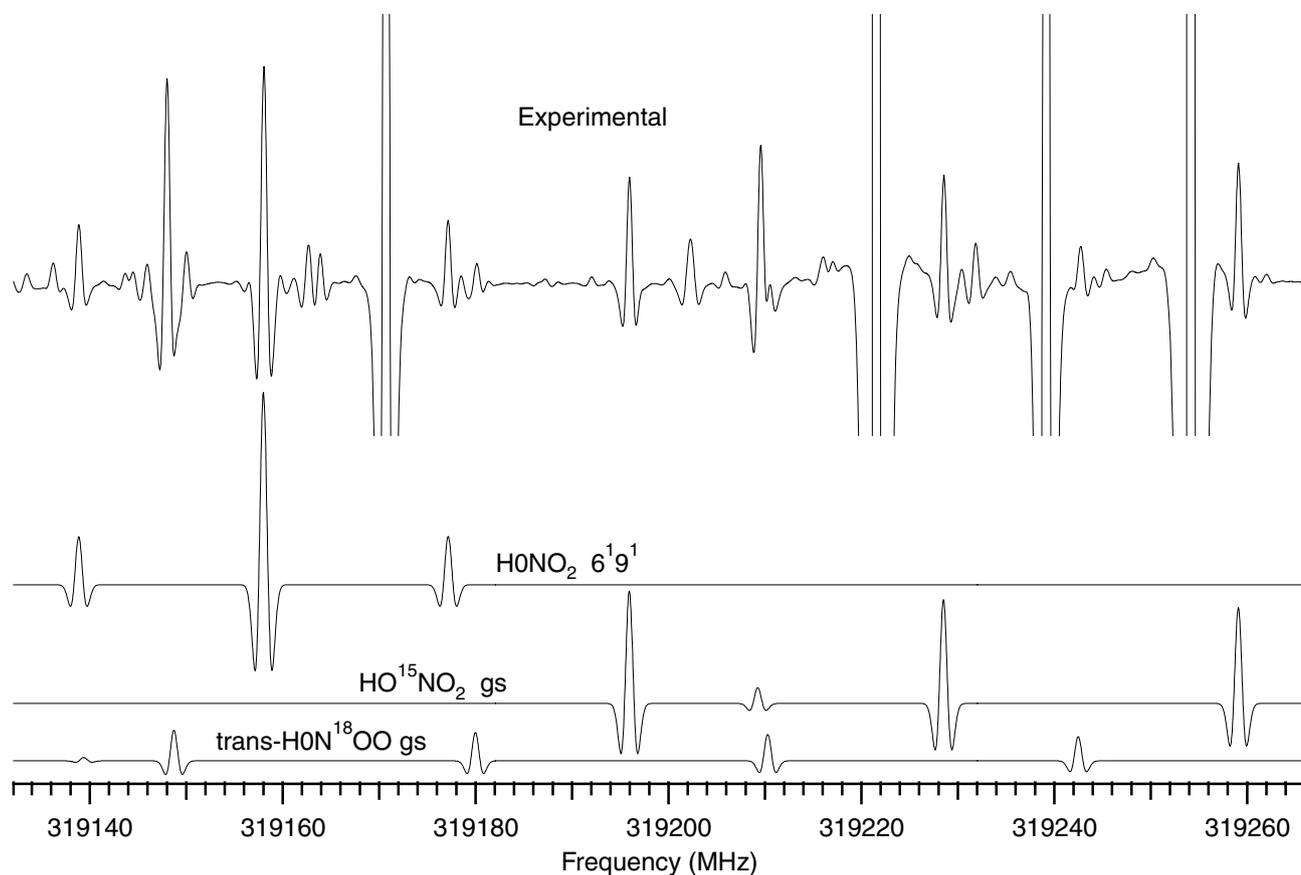


Fig. 2. A portion of the OSU FASSST spectrum of HONO_2 near 319.2 GHz. The simulated spectrum of the $6^1_9^1$ state of the parent species and the ground state of two isotopically substituted species are shown and clearly identified in the spectrum. The gas temperature is ~ 450 K. Note that the abundance of $\text{HO}^{15}\text{NO}_2$ is enhanced by $\sim 2\times$ due to prior experiments using an enriched ^{15}N sample. The strongest lines in the spectrum (with peaks $30\times$ larger than the vertical scale shown) are due to the ground state transitions of the parent species.

Table 2
Data coverage for nitric acid isotopomers

	$\text{HO}^{15}\text{NO}_2$	$\text{trans-HON}^{18}\text{OO}$	$\text{H}^{18}\text{ONO}_2$	$\text{cis-HON}^{18}\text{OO}$	DONO_2
J_{Max}	86	51	55	58	79
$K_{a\text{Max}}$	67	30	29	37	43
ν_{Max} (GHz)	843.5	645.6	644.7	645.2	849.7
N_{meas}	841	211	218	241	443

which was recently characterized up to 600 GHz, no previous millimeter or submillimeter reports were available for nitric acid isotope centrifugal distortion. The extensive analysis of vibrational spectra of $\text{HO}^{15}\text{NO}_2$ [9] had produced centrifugal distortion parameters for the excited vibrational states, however the ground state values were fixed to those calculated from the harmonic force-field in [17].

Rotational constants for the single isotopically substituted nitric acid species have been available since the first structural determination [16]. Since that work did not determine any distortion constants, there is likely to be some error in the accuracy of the parameters (the authors estimate 0.05 MHz). The only discrepancies outside of this range occur for the *cis* and *trans*- ^{18}O isotopologues. Compared to the other ^{18}O isotopologues Cox and Riveros report only 10 transitions for *trans*- ^{18}O , all of which are *a*

type transitions. The sparser data set of this isotopologue is primarily due to the fact that the *b* component of the dipole vector accidentally vanishes. In general, a data set without *b* or *c* type transitions is expected to have limited accuracy for the *A* rotational constant. Indeed, a comparison of the present work with the parameters reported in Cox and Riveros reveals a large (0.47 MHz) discrepancy for the *A* rotational constant of *trans*- ^{18}O . For the *cis*- ^{18}O isotopologue, the errors in the *B* (0.11 MHz change) and *C* (0.61 MHz change) rotational constants are related to the mis-assignment of the $J = 3$ asymmetry doublet.

In their later work, Cox et al. [17] gave quartic centrifugal distortion constants for many rare isotopically substituted nitric acid species. These values, except for DONO_2 , were calculated from the force field and scaled by the available experimental data. Direct comparison

Table 3
Ground state Hamiltonian parameters in MHz for nitric acid isotopomers and isotopologues

Parameter	HO ¹⁵ NO ₂	<i>trans</i> -HON ¹⁸ OO	H ¹⁸ ONO ₂	<i>cis</i> -HON ¹⁸ OO	DONO ₂
A	13012.26285(44)	12715.02740(206)	12970.78329(143)	12318.52820(104)	12970.64807(41)
B	12096.92400(37)	11493.33061(116)	11274.01592(120)	11847.42523(105)	11312.647567(302)
C	6260.13718(32)	6028.29194(91)	6023.16792(82)	6030.79771(81)	6034.940221(231)
− <i>A_J</i>	−8.901231(199)E−03	−7.08513(119)E−03	−8.07089(110)E−03	−9.08143(91)E−03	−6.975710(148)E−03
− <i>A_{JK}</i>	4.49804(37)E−03	3.8990(49)E−03	3.38726(285)E−03	0.01019198(253)	0.45149(39)E−03
− <i>A_K</i>	−7.33847(34)E−03	−0.0126465(95)	−6.0695(53)E−03	−0.0127360(49)	−6.40148(70)E−03
− <i>δ_J</i>	−3.782612(75)E−03	−2.93765(55)E−03	−3.39183(46)E−03	−3.93164(34)E−03	−2.872091(57)E−03
− <i>δ_K</i>	−7.494464(227)E−03	−5.57971(304)E−03	−7.79680(195)E−03	−4.87079(149)E−03	−7.450998(285)E−03
<i>Φ_J</i>	−0.893(34)E−09	−1.57(61)E−09	−2.70(41)E−09	−2.089(309)E−09	−2.4451(260)E−09
<i>Φ_{JK}</i>	0.027599(104)E−06	7.36(267)E−09	0.01013(177)E−06	0.02026(120)E−06	0.053528(176)E−06
<i>Φ_{KJ}</i>	−0.111254(251)E−06	−0.1242(156)E−06	−0.0871(75)E−06	−0.0719(43)E−06	−0.20554(44)E−06
<i>Φ_K</i>	0.121453(197)E−06	0.0990(186)E−06	9.0(103)E−09	0.0104(64)E−06	0.20480(65)E−06
<i>φ_J</i>	−0.0813(151)E−09	−0.510(300)E−09	−0.780(190)E−09	−0.742(136)E−09	−0.9204(112)E−09
<i>φ_{JK}</i>	1.260(102)E−09	−7.3(33)E−09	−3.11(187)E−09	−9.29(146)E−09	0.014851(161)E−06
<i>φ_K</i>	0.051789(102)E−06	0.0502(52)E−06	0.0517(35)E−06	0.04440(142)E−06	0.021293(294)E−06
<i>L_{KKJ}</i>	3.490(44)E−12	0.0249(151)E−09	0.0318(68)E−09	0.0176(32)E−09	3.696(180)E−12
<i>L_K</i>	−3.856(43)E−12	0.0171(173)E−09	0.0237(93)E−09	0.0264(43)E−09	−4.257(236)E−12
<i>l_{JJK}</i>	−0.4976(112)E−12	0.56(76)E−12	−2.06(46)E−12	−0.25(40)E−12	−0.1325(287)E−12
<i>l_{KKJ}</i>	0.7987(176)E−12	−5.71(293)E−12	1.42(200)E−12	6.63(74)E−12	0.569(75)E−12
<i>l_K</i>	−0.1922(227)E−12				
MW AVG	0.002376	−0.006001	−0.000130	−0.005405	0.002306
MW RMS	0.080152	0.075631	0.087995	0.083980	0.052313
<i>σ_{red}</i>	0.80152	0.91190	1.07481	1.04770	0.88247

Table 4
Quartic distortion parameters, all values in kHz

Species	<i>A_J</i>	<i>A_{JK}</i>	<i>A_K</i>	<i>δ_J</i>	<i>δ_K</i>
HO ¹⁵ NO ₂	8.901231(199)	−4.49804(37)	7.33847(34)	3.782612(75)	7.494464(227)
[17]	8.856	−4.584	7.400	3.767	7.530
<i>trans</i> -HON ¹⁸ OO	7.08513(119)	−3.8990(49)	12.6465(95)	2.93765(55)	5.57971(304)
[17]	7.118	−4.251	13.870	2.968	5.580
H ¹⁸ ONO ₂	8.07089(110)	−3.38726(285)	6.0695(53)	3.39183(46)	7.79680(195)
[17]	8.018	−3.141	5.800	3.373	7.962
<i>cis</i> -HON ¹⁸ OO	9.08143(91)	−10.19198(253)	12.7360(49)	3.93164(34)	4.87079(149)
[17]	9.044	−9.833	12.690	3.930	5.168
DONO ₂	6.975710(148)	−0.45149(39)	6.40148(70)	2.872091(57)	7.450998(285)
[17] ^a	6.86(4)	−0.30(33)	6.31(24)	2.89(4)	7.360(130)

Parameters from [17] are converted to the asymmetric form using Table 8.16 in [22].

^a Propagated uncertainties do not include correlation.

requires conversion of the parameters, which are given in the format of the *S* reduced Watsonian, to the *A* format used in the present work. Table 4 shows this comparison for each species in the present work. In a heavy molecule, the dominant effect on rotational and centrifugal distortion terms is typically due to the mass change, and simple scaling relations are useful. However, when oxygen or hydrogen nuclei are substituted in HONO₂, many of the higher order parameters differ significantly, even within the mass equivalent ¹⁸O substituted isotopologues. This is due to the large principal axis rotations that occur. The axis rotation effectively re-maps the force field, typically given in normal coordinates, when it is projected onto the principal inertial axis system and reduced to the determinable Watson type parameters. The accuracy of the scaled force field method is 1–10%, with the worst differences appearing for the *cis* and *trans*-¹⁸O isotopologues. This is remarkably

good agreement considering the number of unknowns and demonstrates the quality of the harmonic force-field and molecular structure in [17,18].

With the large sampling of quanta in the current data set the parameters are determined to much higher accuracy than previous work. The only comparable parameter set is that given by Chou et al. for DONO₂, which includes parameters through sixth order. The present work is only a modest refinement of that effort. Given the full set of isotopic quartic and sextic parameters for the singly substituted isotopic species, an improvement of the molecular force field is possible.

4. Conclusion

This study improves the spectroscopic database for nitric acid, a species known to be important in stratospheric chemical cycles. Spectral features many orders of magni-

tude weaker than the target transitions for remote sensing are now reliably predicted throughout the rotational band.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (<http://msa.lib.ohio-state.edu/jmsa_hp.htm>).

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