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Quartic force field-derived vibrational frequencies and spectroscopic constants for the isomeric pair SNO and OSN and isotopologues

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The SNO and OSN radical isomers are likely to be of significance in atmospheric and astrochemistry, but very little is known about their gas phase spectroscopic properties. State-of-the-art *ab initio* composite quartic force fields are employed to analyze the rovibrational features for both systems. Comparison to condensed-phase experimental data for SNO has shown that the 1566.4 cm^{-1} ν_1 N–O stretch is indeed exceptionally bright and likely located in this vicinity for subsequent gas phase experimental analysis. The OSN ν_1 at 1209.4 cm^{-1} is better described as the antisymmetric stretch in this molecule and is also quite bright. The full vibrational, rotational, and rovibrational data are provided for SNO and OSN and their single ^{15}N , ^{18}O , and ^{34}S isotopic substitutions in order to give a more complete picture as to the chemical physics of these molecules. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929472>]

I. INTRODUCTION

NO_2 is an unmistakably important atmospheric molecule belonging to the NO_x (“nox”) family of atmospheric pollutants. Additionally, sulfur-oxygen compounds are known pollutants, as well, originating from natural as well as man-made sources. Hence, the inclusion of sulfur in nox-like molecules and nitrogen in sulfoxide compounds has garnered much interest in the atmospheric chemistry community for some time.^{1–7} However, such interest does not stop with Earth’s atmosphere. The sulfur-rich atmosphere of Venus is also a tantalizing location for the study molecular species containing nitrogen, oxygen, and sulfur atoms,^{8,9} but there is no need to limit such study to standard pressures. Extending beyond our own solar system, the interstellar medium (ISM) is known to possess dozens of small molecules in regions as diverse as circumstellar envelopes, giant molecular clouds, and even the diffuse ISM.¹⁰ In fact, nitric oxide was detected in 1978 toward gas cloud Sagittarius B2(N) and, as a result, also the center of galaxy.¹¹ Furthermore, this detection is preceded by the telescopic spectral isolation of SO and SO_2 five and three, respectively, years prior to NO.^{12,13} As a result, molecules of the [N, O, S] family are likely of significance in each of these environments ranging from the tangible to the remote.

The simplest molecules of this class are the three triatomics: SNO, OSN, and NOS. SNO was first observed in the laboratory in 1975 by Tchir and Spratley from photolysis reactions of *cis*-HNSO isolated in argon matrices.^{1,2} The two highest frequency modes of SNO were assigned to bands in the resulting infrared spectrum at 1523.0 cm^{-1} (ν_1) and 789.7 (ν_3) cm^{-1} ,¹ while a band at 1195 cm^{-1} was assigned to the SO stretch of OSN.² The 1523.0 cm^{-1} band of SNO and 1195 cm^{-1} band of OSN are strong absorbers indicating that they likely

result from stretches involving the oxygen atom. Subsequent matrix isolation studies^{3,4} have largely corroborated the earlier work adding knowledge of the SNO overtone for the ν_3 band at 1596.4 cm^{-1} clearly indicating a type-1 Fermi resonance present between $2\nu_3$ and ν_1 . Also, it appears as though SNO and OSN are significant products in fragmentation reactions of [H, N, O, S] tetraatomic species.⁷

The known spectroscopic data for SNO and OSN have been included in atmospheric models of the Venusian atmosphere,^{8,9} but it has yet to be established where else these simple molecular radicals may arise. To this point in time, there exists little experimental data on the gas phase spectral features of SNO and OSN, the only experimentally observed [N, O, S] isomers. Theoretical data have been produced for SNO including electronic excitations and rotational data,¹⁴ but the vibrationally excited rotational analysis of SNO as well as predictions for the sextic rotational constants has not been previously undertaken with almost no spectral data available for OSN. Such information is necessary for any atmospheric or interstellar studies related to these systems.

Fortunately, highly accurate *ab initio* quantum chemical methods are beginning to produce spectroscopically meaningful data to assist with such applied research. The use of quartic force fields (QFFs) in spectroscopic analysis has recently provided exceptional comparison to experiment for rotational constants ($<0.2\%$) and fundamental vibrational frequencies with some studies reporting hydride stretches to as good as 1.0 cm^{-1} as compared to experiment.^{15–20} QFFs are fourth-order Taylor series expansions of the potential portion of the nuclear Hamiltonian which may then be utilized in solving the nuclear Schrödinger equation. QFFs are of the form

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l, \quad (1)$$

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where Δ_i are displacements along a chosen set of coordinates, and the $F_{ij\dots}$ are the force constants of unrestricted i, j, k, l indices. Coupling second-order vibrational perturbation theory (VPT2)^{21,22} and rotational perturbation theory²³ to such a potential surface can provide a full range of vibrational and rovibrational data necessary to describe more fully the system of interest. There has been much success recently in the analysis of the *cis*- and *trans*-HOCO radicals,^{24,25} the HSCO and HOCS analogues,²⁶ and in noble gas polyhydrides^{27,28} from QFFs in order to provide a deeper understanding of these important but experimentally transient systems. This same approach is applied here for the SNO and OSN radical isomers.

II. COMPUTATIONAL DETAILS

All electronic structure computations in this work make use of the restricted-open shell Hartree-Fock reference wavefunction,^{29–31} coupled cluster theory at the singles, doubles, and perturbative triples [CCSD(T)] level,³² and the MOLPRO 2010.1 quantum chemistry program.³³ The two exceptions are the double-harmonic fundamental vibrational frequency intensities. These are computed by MP2/aug-cc-pVTZ with the Gaussian09 program.^{34,35}

In keeping with the proven methodology for composite energy QFFs,^{36,37} the reference geometry is optimized with the aug-cc-pV5Z basis set,^{38,39} where the additional $(5 + d)$ functions are included for the sulfur atom and are implied in the basis description for the remainder of the discussion. Corrections to this geometry are made for core correlation by using the Martin-Taylor (MT) core correlating basis set⁴⁰ in two geometry optimizations: one including the core electrons and one without. The differences in the subsequent optimized geometric parameters are then added to the CCSD(T)/aug-cc-pV5Z results.

From this reference, a grid of 129 points is generated for each isomer. The points are used to fully define Eq. (1). For SNO, coordinate 1 is the S–N bond length, coordinate 2 is the N–O bond, and coordinate 3 is the bond angle. Similarly for OSN, coordinate 1 is the O–S bond, coordinate 2 is the S–N bond, and coordinate 3 is the bond angle. At each point, the CCSD(T)/aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z energies are computed and extrapolated to the complete basis set (CBS) limit via a three-point formula.⁴¹ Subsequently, composite corrections are made, again, for core correlation with the MT bases and for scalar relativity through the Douglas-Kroll formulation⁴² and are added to the CBS energy. The use of these three terms (CBS, core correlation, and relativity) produces the abbreviated CcCR QFF.²⁴ For all of the electronic structure computations, the T_1 diagnostics are very close to 0.03, small enough to justify the use of single-reference wave functions.⁴³

Fitting of these points through a least-squares procedure produces the equilibrium geometry. Refitting the surface with the new minimum gives zero values for the gradients and properly defined quartic, cubic, and quadratic force constants. Transformation of these force constants from simple-internal to Cartesian coordinates is done through the INTDER program.⁴⁴ The SPECTRO program⁴⁵ uses the force constants determined from the CcCR QFF to compute the VPT2

TABLE I. The SNO CcCR simple-internal force constants (in mdyn/ $\text{\AA}^n \text{ rad}^m$).

F_{11}	9.922 778	F_{221}	50.2859	F_{1111}	214.70	F_{3222}	505.29
F_{21}	−7.165 595	F_{222}	−67.6865	F_{2111}	−82.76	F_{3311}	533.84
F_{22}	10.294 493	F_{311}	−62.2585	F_{2211}	148.05	F_{3321}	−526.41
F_{31}	−7.370 578	F_{321}	74.3558	F_{2221}	−227.54	F_{3322}	509.68
F_{32}	9.959 533	F_{322}	−81.5470	F_{2222}	333.68	F_{3331}	−293.23
F_{33}	15.219 040	F_{331}	86.7136	F_{3111}	−316.43	F_{3332}	239.58
F_{111}	−7.740 3	F_{332}	−72.6792	F_{3211}	388.72	F_{3333}	293.11
F_{211}	−37.111 0	F_{333}	−10.6547	F_{3221}	−454.41		

frequencies and the spectroscopic constants. In so doing, SNO requires input of the $2\nu_3 = \nu_1$ type-1 Fermi resonance, and OSN requires the $\nu_3 + \nu_2 = \nu_1$ type-2 Fermi resonance.

III. RESULTS AND DISCUSSION

A. SNO

The force constants for SNO are given in Table I and are determined from a fit with a sum of residuals squared on the order of 10^{-16} a.u.². Since the bond strengths are largely proportional to the diagonal, harmonic force constants, it is interesting to note that the S–N bond is roughly equal to the strength of the N–O bond. However, the S–N bond length is significantly longer at 1.584 201 \AA than the N–O bond of 1.191 203 \AA as given for the vibrationally averaged (R_a) bond lengths in Table II. The cubic and quartic force constants from Table I are notably larger than any others computed with a similar methodology. Within the Born-Oppenheimer approximation, the equilibrium geometrical values remain the same among isotopologues, but the vibrationally averaged values will change. Replacement of standard ^{32}S with ^{34}S , for instance, decreases the S–N bond by 0.000 059 \AA while the N–O bond length and $\angle(\text{S–N–O})$ remain largely unchanged. Inclusion of ^{15}N or ^{18}O also affects the geometries and, subsequently, the vibrationally averaged rotational constants.

The SNO equilibrium rotational constants, also given in Table II, are in line with those determined previously.¹⁴ Hence, A_0 , B_0 , and C_0 should be reliable, theoretically improved values, especially for the B– and C–type constants. This molecule has fairly significant linear character due to the 140.083° bond angle, and the presence of the heavier sulfur atom at the end of the molecule. B_0 and C_0 differ by 0.006 159 cm^{-1} , and A_0 is nearly 40× larger. Isotopic substitution drops every rotational constant in every case highlighting strong distinguishability with high-resolution techniques for each isotopologue. The quartic and sextic distortion constants are provided in each case. Comparison between the standard SNO CcCR QFF D_x constants and those from Ref. 14 is fairly good. Even though the D_K values differ by a factor of two, they are still within the same order of magnitude. It has been shown that some D–type constants computed with the current methodology can be in error by as much as 40% for those that are anharmonically affected.⁴⁶ However, most are in error by less than 10%.⁴⁷ There is no reason to suspect such an issue with SNO insinuating that the distortion constants provided herein should be experimentally meaningful. The dipole moment is 0.77 D.

TABLE II. The CcCR QFF equilibrium and zero-point (R_α) geometries, vibrational frequencies and intensities,^a and spectroscopic constants for SNO and isotopologues.

	SNO	Previous ^b	³⁴ SNO	S ¹⁵ NO	SN ¹⁸ O
r_0 (S–N) Å	1.584 201		1.584 140	1.584 109	1.584 198
r_0 (N–O) Å	1.191 203		1.191 204	1.191 148	1.191 104
\angle (S–N–O)	140.083		140.083	140.080	140.078
A_0 cm ^{−1}	7.974 055		7.948 274	7.582 525	7.775 568
B_0 cm ^{−1}	0.218 172		0.212 648	0.217 474	0.205 162
C_0 cm ^{−1}	0.212 013		0.206 775	0.211 056	0.199 575
A_1 cm ^{−1}	7.837 744		7.812 600	7.458 355	7.639 702
B_1 cm ^{−1}	0.217 264		0.211 768	0.216 611	0.204 282
C_1 cm ^{−1}	0.211 086		0.205 877	0.210 173	0.198 679
A_2 cm ^{−1}	8.091 859		8.074 445	7.671 725	7.909 558
B_2 cm ^{−1}	0.216 775		0.211 291	0.216 106	0.203 876
C_2 cm ^{−1}	0.210 666		0.205 465	0.209 740	0.198 332
A_3 cm ^{−1}	8.575 618		8.538 059	8.159 196	8.338 603
B_3 cm ^{−1}	0.218 046		0.212 528	0.217 342	0.205 055
C_3 cm ^{−1}	0.211 730		0.206 505	0.210 764	0.199 329
D_J kHz	2.553	2.187	2.432	2.525	2.262
D_{JK} MHz	−0.443	−0.2781	−0.431	−0.408	−0.425
D_K MHz	142.446	245.22	141.422	128.884	136.027
d_1 kHz	−0.169	−0.1136	−0.158	−0.174	−0.148
d_2 Hz	−3.922		−3.588	−4.263	−3.193
H_J mHz	0.974		0.893	0.911	0.900
H_{JK} Hz	−0.046		−0.039	−0.086	−0.016
H_{KJ} Hz	−109.504		−105.961	−96.626	−101.733
H_K kHz	31.898		31.556	27.456	29.760
h_1 mHz	0.372		0.338	0.375	0.311
h_2 mHz	0.019		0.017	0.020	0.015
h_3 mHz	0.005		0.005	0.006	0.004
r_e (S–N) Å	1.579 358	1.5809
r_e (N–O) Å	1.187 812	1.1918
\angle (S–N–O)	139.916	139.97
A_e MHz	7.682 526	7.6640	7.658 132	7.311 674	7.494 988
B_e MHz	0.219 385	0.218	0.213 824	0.218 652	0.206 297
C_e MHz	0.213 294	0.212	0.208 016	0.212 303	0.200 771
μ_x D	−0.77	
μ_y D	0.04	
μ^c D	0.77	
Harmonic zero-point cm ^{−1}	1 482.8		1 476.9	1 456.8	1 453.9
ω_1 cm ^{−1} N–O	1 620.2 (371)	1 639.3	1 620.2	1 589.3	1 581.5
ω_2 cm ^{−1} bend	518.1 (1)	489.8	515.3	510.4	506.4
ω_3 cm ^{−1} N–S	827.3 (13)	754.5	818.3	813.9	820.0
Zero-point cm ^{−1}	1 481.6		1 475.7	1 455.6	1 452.8
ν_1 cm ^{−1} N–O	1 566.4	1 630.7/1 522.8 ^d /1 527.2 ^e	1 558.2 ^f	1 540.6	1 536.5
ν_2 cm ^{−1} bend	524.5	514.5	521.6	516.6	512.4
ν_3 cm ^{−1} N–S	812.8	792.6/790.2 ^d /792.3 ^e	804.2	799.8	805.7
$2\nu_1$ cm ^{−1}	3 172.4		3 172.0	3 113.2	3 098.4
$2\nu_2$ cm ^{−1}	1 055.4	1 025.2	1 049.6	1 039.8	1 031.1
$2\nu_3$ cm ^{−1}	1 645.1	1 558.2/1 596.4 ^d /1 601.1 ^e	1 636.1 ^f	1 615.3	1 623.4
$\nu_1 + \nu_2$ cm ^{−1}	2 130.8	2 139.7	2 127.4	2 093.0	2 080.6
$\nu_1 + \nu_3$ cm ^{−1}	2 417.8	2 455.4	2 409.0	2 374.6	2 372.5
$\nu_2 + \nu_3$ cm ^{−1}	1 330.3	1 303.7	1 319.0	1 309.8	1 311.1
α^A 1 MHz	4 086.5	11 982.7	4 067.4	3 722.5	4 073.2
α^A 2 MHz	−3 531.7	−5 420.29	−3 782.5	−2 674.2	−4 016.9
α^A 3 MHz	−18 034.4	−42 006.9	−17 681.3	−17 288.2	−16 879.4
α^B 1 MHz	27.2	21.7	26.4	25.9	26.4
α^B 2 MHz	41.9	25.2	40.7	41.0	38.6
α^B 3 MHz	3.8	3.6	3.6	3.9	3.2

TABLE II. (Continued.)

	SNO	Previous ^b	³⁴ SNO	S ¹⁵ NO	SN ¹⁸ O
α^C 1 MHz	27.8	15.4	26.9	26.5	26.9
α^C 2 MHz	40.4	30.4	39.3	39.5	37.3
α^C 3 MHz	8.5	6.4	8.1	8.7	7.4

^aThe MP2/aug-cc-pVTZ double harmonic intensities are in parentheses beside the harmonic frequency of the standard isotopologue and given in km/mol.

^bRCCSD(T)-F12/cc-pVTZ-F12 3D PES data SURFIT results from Ref. 14.

^cThe SNO coordinates (in Å with the center-of-mass at the origin) used to generate the CCSD(T)/aug-cc-pVTZ Born-Oppenheimer dipole moment component are S, -1.016 576, 0.060 923, 0.000 000; N, 0.511 738, -0.337 362, 0.000 000; O, 1.584 012, 0.173 572, 0.000 000.

^dAr-matrix data from Ref. 4.

^eAr-matrix data from Ref. 5.

^fThe $2\nu_3 = \nu_1$ Fermi resonance leads to significant mixing in these states. These are hand-assigned and differ from the SPECTRO assignments.

The harmonic and anharmonic vibrational frequencies are also given in Table II. The most intense transition is ω_1 , the N–O stretch, with a double-harmonic intensity of 371 km/mol. The bend has almost no intensity explaining why it has not been observed in any experiments to date: Ar-matrix or gas phase. The intensities computed here are congruent with the “strong” and “medium” labels given to the ν_1 and ν_3 modes, respectively, by Tchir and Spratley¹ and confirmed by Andrews and coworkers.⁴ The ν_1 and ν_3 modes shift expectedly downward from their harmonic brethren, but ν_2 increases to 524.5 cm⁻¹ from $\omega_2 = 518.1$ cm⁻¹. Small positive anharmonicities are well-known for other low-frequency modes of similar molecules.¹⁶ Additionally, comparison between the theoretical gas phase values and the Ar-matrix condensed phase values also compares expectedly^{24,25,48} with the CcCR ν_1 at 1566.4 cm⁻¹ and the Ar-matrix ν_1 at 1527.2 cm⁻¹ (Ref. 5). The two-quanta overtones and combination bands are also given in Table II within similar comparison between the computed and condensed phase frequency of $2\nu_3$, 1645.1 cm⁻¹ versus 1601.1 cm⁻¹, respectively.

The prediction of overtones and combination bands becomes less reliable than fundamentals for QFFs since small errors in the fundamentals can compound in the higher-quanta modes.⁴⁹ Even so, the assignment of the ν_1 versus the $2\nu_3$ modes is still unclear. There is no doubt that significant mixing and Fermi resonances are taking place for these two modes, but previous experiment^{4,5} has assigned the lower frequency mode to ν_1 and the higher frequency mode to $2\nu_3$ as is given in Table II. Theoretical work by Yazidi and coworkers¹⁴ has inverted that assignment with the admission that significant mixing is taking place. The established CcCR VPT2 methodology utilized here approaches the problem differently than the variational results from Yazidi and coworkers. VPT2 actually agrees with the assignments from the condensed phase experiment. Again, there is significant mixing between the two states in the nuclear wavefunction. In fact, the $2\nu_3 = \nu_1$ type-2 Fermi resonance creates issues with the involved modes for ³⁴SNO. Even though SPECTRO assigns the 1636.1 cm⁻¹ frequency to ν_1 and the 1558.2 cm⁻¹ frequency to $2\nu_3$, we have chosen to reverse this assignment due to patterns present from the other isotopologues. The clearest way to tell the difference in gas phase results will come from the intensities. As stated previously, the N–O stretch will be extremely bright. The $2\nu_3$ will be significantly dimmer.

The same sets of harmonic fundamentals, anharmonic fundamentals, zero-point energies, and two quanta frequencies

are also given for ³⁴SNO, S¹⁵NO, and SN¹⁸O in Table II. The vibrationally averaged rotational constants for the fundamental vibrational frequencies are also given in this table in order to provide a complete set of rovibrational spectroscopic data for the community.

B. OSN

The force constants for OSN given in Table III differ from those in Table I most notably in that while the O–S force constant (F_{11}) is of similar magnitude as the S–N force constant (F_{11}) in SNO, the S–N force constant (F_{22}) in OSN is nearly half this value. However, the OSN bond lengths (Table IV) are nearly equal to one another at 1.449 084 Å and 1.493 341 Å, respective of O–S and S–N. Both cases are opposite of the trends noted for SNO. The bond lengths are not surprising since sulfur is central to this atom, and the second-row atoms (N and O) are on the extremities. OSN is significantly less linear in nature than SNO since the former has a bond angle of 125.186°. Additionally, the A-type rotational constant is an order of magnitude larger than the B- and C-type constants, but the differences between the two groups are less than SNO and greater between B_0 and C_0 in OSN. Similar trends are present in the rotational constants for OSN for single-isotopic substitution as they are in SNO. The equilibrium quartic and sextic distortion constants are also provided for OSN and each of its isotopologues. The 1.19 D dipole moment is larger here for OSN than the dipole moment in SNO.

It is interesting to note that the OSN isomer is actually more thermodynamically stable than the seemingly more common SNO radical. OSN is 2.67 kcal/mol (934 cm⁻¹) lower in energy on the [N, O, S] potential energy surface. The anharmonic zero-point energy for OSN is given in Table IV as

TABLE III. The CcCR OSN simple-internal force constants (in mdyn/Åⁿ rad^m).

F ₁₁	11.315 341	F ₂₂₁	19.0649	F ₁₁₁₁	295.93	F ₃₂₂₂	236.08
F ₂₁	-3.848 571	F ₂₂₂	-33.8747	F ₂₁₁₁	17.12	F ₃₃₁₁	229.58
F ₂₂	6.000 068	F ₃₁₁	-22.7379	F ₂₂₁₁	15.36	F ₃₃₂₁	-273.65
F ₃₁	-3.850 896	F ₃₂₁	34.8992	F ₂₂₂₁	-66.11	F ₃₃₂₂	285.98
F ₃₂	6.193 203	F ₃₂₂	-44.6414	F ₂₂₂₂	138.39	F ₃₃₃₁	-280.59
F ₃₃	8.176 891	F ₃₃₁	41.6180	F ₃₁₁₁	-60.34	F ₃₃₃₂	297.98
F ₁₁₁	-61.999 2	F ₃₃₂	-43.7392	F ₃₂₁₁	124.25	F ₃₃₃₃	429.51
F ₂₁₁	-7.773 0	F ₃₃₃	-29.9257	F ₃₂₂₁	-185.15		

TABLE IV. The OSN equilibrium and zero-point (R_α) geometries, vibrational frequencies and intensities,^a and spectroscopic constants from the CcCR QFF.

	OSN	Previous	¹⁸ OSN	O ³⁴ SN	OS ¹⁵ N
r_0 (O–S) Å	1.449 084		1.448 975	1.449 050	1.449 048
r_0 (S–N) Å	1.493 341		1.493 308	1.493 308	1.493 254
\angle (O–S–N)	125.186		125.183	125.119	125.191
A_0 cm ^{−1}	2.428 320		2.361 455	2.359 127	2.385 140
B_0 cm ^{−1}	0.331 197		0.312 366	0.331 189	0.319 856
C_0 cm ^{−1}	0.290 262		0.274 797	0.289 227	0.280 915
A_1 cm ^{−1}	2.379 076		2.306 492	2.313 220	2.340 132
B_1 cm ^{−1}	0.330 463		0.311 831	0.330 438	0.319 105
C_1 cm ^{−1}	0.289 046		0.273 394	0.288 013	0.279 757
A_2 cm ^{−1}	2.423 651		2.364 601	2.352 623	2.378 668
B_2 cm ^{−1}	0.329 604		0.310 754	0.329 656	0.318 363
C_2 cm ^{−1}	0.288 897		0.273 511	0.287 890	0.279 603
A_3 cm ^{−1}	2.516 090		2.444 909	2.443 965	2.470 065
B_3 cm ^{−1}	0.332 634		0.313 700	0.332 598	0.321 240
C_3 cm ^{−1}	0.290 309		0.274 863	0.289 246	0.280 976
D_J kHz	9.692		8.721	9.626	9.036
D_{JK} MHz	−0.461		−0.434	−0.441	−0.437
D_K MHz	14.770		13.999	13.953	14.220
d_1 kHz	−3.032		−2.679	−3.064	−2.794
d_2 kHz	−0.089		−0.076	−0.090	−0.083
H_J mHz	64.345		54.292	64.172	57.900
H_{JK} Hz	−4.069		−3.360	−4.083	−3.658
H_{KJ} Hz	−225.186		−208.606	−208.619	−209.185
H_K kHz	9.285		8.571	8.519	8.769
h_1 mHz	30.960		26.014	30.959	27.687
h_2 mHz	1.756		1.463	1.735	1.626
h_3 mHz	1.660		1.297	1.770	1.442
r_e (O–S) Å	1.444 957	
r_e (S–N) Å	1.489 098	
\angle (O–S–N)	125.412	
A_e MHz	2.411 392		2.345 637	2.342 915	2.368 418
B_e MHz	0.331 633		0.312 765	0.331 618	0.320 279
C_e MHz	0.291 538		0.275 968	0.290 500	0.282 127
μ_x D	0.05	
μ_y D	−1.18	
μ^b D	1.19	
Harmonic zero-point cm ^{−1}	1276.6		1250.9	1265.4	1261.7
ω_1 cm ^{−1} antisymmetric	1233.7 (282)		1204.7	1218.4	1228.7
ω_2 cm ^{−1} bend	298.1 (31)		292.7	295.0	294.9
ω_3 cm ^{−1} symmetric	1021.4 (14)		1004.5	1017.4	999.7
Zero-point cm ^{−1}	1273.5		1248.0	1262.3	1258.5
ν_1 cm ^{−1} antisymmetric	1209.2	1195 ^c	1181.8	1194.6	1203.9
ν_2 cm ^{−1} bend	302.1		296.7	298.9	298.7
ν_3 cm ^{−1} symmetric	1010.7		993.8	1006.7	989.7
$2\nu_1$ cm ^{−1}	2404.7		2350.4	2375.7	2394.6
$2\nu_2$ cm ^{−1}	606.8		595.8	600.3	600.0
$2\nu_3$ cm ^{−1}	2012.5		1980.3	2004.4	1970.3
$\nu_1 + \nu_2$ cm ^{−1}	1509.6		1477.3	1491.7	1501.0
$\nu_1 + \nu_3$ cm ^{−1}	2211.6		2165.1	2193.1	2187.3
$\nu_2 + \nu_3$ cm ^{−1}	1320.2		1296.6	1312.6	1296.5
α^A 1 MHz	1476.3		1647.7	1376.3	1349.3
α^A 2 MHz	140.0		−94.3	195.0	194.0
α^A 3 MHz	−2631.3		−2501.9	−2543.4	−2546.0
α^B 1 MHz	22.0		16.0	22.5	22.5
α^B 2 MHz	47.7		48.3	46.0	44.8
α^B 3 MHz	−43.1		−40.0	−42.2	−41.5
α^C 1 MHz	36.5		33.1	36.4	34.7

TABLE IV. (Continued.)

	OSN	Previous	¹⁸ OSN	O ³⁴ SN	OS ¹⁵ N
α^C 2 MHz	40.9		38.6	40.1	39.3
α^C 3 MHz	-1.4		-2.0	-0.6	-1.8

^aThe MP2/aug-cc-pVTZ double harmonic intensities are in parentheses beside the harmonic frequency of the standard isotopologue and given in km/mol.

^bThe OSN coordinates (in Å with the center-of-mass at the origin) used to generate the CCSD(T)/aug-cc-pVTZ Born-Oppenheimer dipole moment component are O, -1.253 973, 0.328 635, 0.000 000; S, 0.034 651, -0.325 084, 0.000 000; N, 1.353 225, 0.366 855, 0.000 000.

^cAr-Matrix phase results from Ref. 2.

1276.6 cm⁻¹, 341 cm⁻¹ above the SNO minimum. Hence, SNO may actually be a preferred kinetic product in the reactions that create [N, O, S] species since it is not the thermodynamic minimum.

The vibrational frequencies for OSN have previously been labelled as the S–O and S–N stretches, but the anharmonic analysis shows that a better description may actually be the symmetric and antisymmetric stretches that one would find in the analogous SO₂ molecule.⁵⁰ Even though nitrogen is less massive than oxygen, the relative masses for each atom compared to sulfur are not significantly different, especially for inclusion of ¹⁵N. Such a labeling is further corroborated by the double-harmonic intensities. The ω_1 double-harmonic intensity is 282 km/mol. The ω_3 intensity is 14 km/mol. The two stretching frequencies also differ by roughly 200 cm⁻¹ showing that they are of similar construction as one would expect for symmetric and antisymmetric stretching pairs. The low-energy bend is much brighter for OSN than for SNO, where the OSN bend should be much more visible.

The anharmonic frequencies from Table IV shift expectedly from the anharmonic values with the ν_2 bend once more giving a slight positive anharmonicity. The 1209.2 cm⁻¹ CcCR QFF ν_1 is in the right range as the original 1195 cm⁻¹ Ar-matrix detection.² As such, it appears as though the original assignment is valid. Again, the actual label may not be complete. Even though these ν_1 and ν_3 frequencies in OSN are roughly 150 cm⁻¹ less than the corresponding frequencies in SO₂, the difference between symmetric and antisymmetric S–O stretches therein is about 200 cm⁻¹.⁵⁰ For OSN ν_1 and ν_3 , the frequency difference is 198.5 cm⁻¹ adding further credence to the description of these two modes as symmetric and antisymmetric pairs. The ν_2 bend is quite low at 302.1 cm⁻¹. The two quanta overtones and combination bands round out the vibrational data, and the rotational constants for each vibrational state are also provided here for OSN. The isotopologue frequencies and rovibrational data give a complete picture of this system in order to assist in subsequent spectral analysis of this molecule whether in the laboratory, atmosphere, or beyond.

IV. CONCLUSIONS

Even though equilibrium OSN is slightly lower in energy than SNO, SNO has the most experimental and computational data available. This may be due to kinetic effects as opposed to thermodynamic considerations. Comparison of the previous experimental data to the CcCR QFF results lends credence to the assignments of the SNO ν_1 and $2\nu_3$ modes in the Ar-matrix which are different from the theoretical assignments of Yazidi

and coworkers.¹⁴ The intensities computed here also show that the ν_2 bend was not observed in these experiments due to its very low intensity. Additionally, the CcCR VPT2 frequencies for both SNO and OSN compare to the condensed-phase data expectedly giving reason to believe that the CcCR frequencies should also be within 5–15 cm⁻¹ of gas phase experiment as has been noted in the previous benchmarks with the same methodology. Furthermore, OSN has behavior akin to that of a C_{2v} molecule such as the closely related SO₂ system known to exist in planetary atmospheres as well as in the ISM. The relative masses of nitrogen and oxygen compared to sulfur are similar giving it more symmetric behavior than planar SNO. Finally, spectroscopic data for OSN and its isotopologues have been provided here for the first time, and a more complete description of SNO and its isotopologues is also given. Hence, the presence of OSN and SNO may yet be confirmed in the atmosphere or ISM since accurate theoretical data are now available.

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