Protonated Nitrous Oxide, $NNOH^+$: Fundamental Vibrational Frequencies and Spectroscopic Constants from Quartic Force Fields

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(Dated: July 23, 2013)

Abstract

The interstellar presence of protonated nitrous oxide has been suspected for some time. Using established high-accuracy quantum chemical techniques, spectroscopic constants and fundamental vibrational frequencies are provided for the lower energy O-protonated isomer of this cation and its deuterated isotopologue. The vibrationally-averaged B_0 and C_0 rotational constants are within 6 MHz of their experimental values and the D_J quartic distortion constants agree with experiment to within 3%. The known gas phase O−H stretch of $NNOH^+$ is 3330.91 cm^{-1}, and the vibrational configuration interaction computed result is 3330.9 cm^{-1}. Other spectroscopic constants are also provided, as are the rest of the fundamental vibrational frequencies for $NNOH^+$ and its deuterated isotopologue. This high-accuracy data should serve to better inform future observational or experimental studies of the rovibrational bands of protonated nitrous oxide in the ISM and the laboratory.

I. INTRODUCTION

It has been long-believed that protonated nitrous oxide should be present in the interstellar medium (ISM).[1] Currently, this cation has not yet been detected in the ISM, but the molecular precursor, N_2O, has been observed in the giant molecular cloud Sagittarius B2.[2] Reaction schemes necessary to create protonated nitrous oxide and its isotopologue are believed to be closely related to those that to lead to the formation of $HOCO^+$,[3] which has also been previously detected in the ISM.[4] There are two distinct isomers present on the protonated nitrous oxide potential energy surface, and various charge transfer reactions leading to the creation of either isomer are possible in the ISM and other astronomically-relevant environments.[5]

In 1986, an initial study into this molecular system was able to deduce rotational and quartic distortion constants for at least one of the isomers in the ground vibrational state and the $v = 1$ for the ν_1 hydrogen-stretch, but it was still uncertain as to which isomer was present.[6] Shortly thereafter, Bogey *et al.*[1] corroborated the ground vibrational state data but was not able to provide any more insight into the molecular structure. Initial theoretical examinations indicated that the O-protonated isomer is the more energetically stable of the two.[7] Furthermore, the equilibrium rotational constants of $NNOH^+$ computed in the same study more closely resemble those from the experiments than do the equilibrium $HNNO^+$ rotational constants. Later experimental work[8] strengthened the conclusion that $NNOH^+$ was the isomer observed. Further theoretical study utilized a myriad of methods to determine the same result unequivocally,[9] and modern experiments also agree.[10,11] Recent, highly-accurate computations report the O-protonated isomer ($NNOH^+$) to be 4.02 kcal/mol lower in energy than the N-protonated isomer ($HNNO^+$), and the transition state between the two is 86.06 kcal/mol above the $NNOH^+$ minimum.[11]

The ν_1 O−H stretching fundamental vibrational frequency was first successfully measured at 3330.91 cm^{-1} in the initial study undertaken by Amano[6]. Ne matrix-isolation data has since followed[12] and shows a red-shift of 43.3 cm^{-1} in this fundamental frequency. $NNOD^+$ was measured in the same Ne matrix setup, and the O−D fundamental is reported to be 2426.3 cm^{-1}. However, none of the other fundamental vibrational frequencies have been measured experimentally in either the gas phase or in matrix studies. Computations have also been limited to the harmonic approximation,[9,12] and further refinement to these values has not been provided in the literature.

The vibrational and rotational properties of several tetra-atomic, monohydrogen, linear/quasilinear cations of interstellar significance have been examined by our group recently through the use of quartic force fields (QFFs). Cations included are: $HOCO^+$ (Ref. 13), $HSCO^+$/$HOCS^+$ (Ref. 14), and l-C_3H^+ (Ref. 15), where accuracies compared to experiment for many of the known spectroscopic quantities have been better than 0.1%. Additionally, recent work on isocyanic acid,[16] which is isoelectronic to $NNOH^+$, has also shown high-accuracy in the use of QFFs. Hence, we are applying the techniques shown previously to produce accurate results for these systems to further elucidate the vibrational frequencies and spectroscopic constants of the lower energy $NNOH^+$ isomer. The reference data generated for $NNOH^+$ are timely for the recent commissioning of the newest generation of space-based and ground-based telescopes including the Atacama Large Millimeter Array (ALMA), the Stratospheric Observatory for Infrared Astronomy (SOFIA), and the upcoming James Webb Space Telescope (JWST), as well as for use in analyzing archived data from completed missions such as the Herschel Space Observatory. This is especially true for observational studies that might use the Echelon-CROSS-Echelle Spectrograph (EXES) instrument on SOFIA, which records high-resolution spectra in the 355 cmi^{-1} to the 2200 cm^{-1} range. Finally, in order to fully characterize the rovibrational spectra of $NNOH^+$ whether for laboratory studies or comparison to astronomical observations, elucidation of reference data such as those provided in this work are essential, especially in the vibrational frequency regime.

II. COMPUTATIONAL DETAILS

The basic procedure utilized here has been extensively described in Refs. 17–19, as well as Ref. 13 for quasi-linear molecules of this type. In brief, the reference geometry is determined utilizing RHF-CCSD(T) (Refs. 20–22) with a three-point cc-pVTZ, cc-pVQZ, and cc-pV5Z basis set[23–25] extrapolation[27] corrected for core-correlation from the cc-pCVTZ basis set and scalar relativity[28] using the cc-pVTZ-DK basis set. From this point, 743 symmetry-unique displacements are generated for coordinates composed of the three bond lengths, $\angle$H$-$O$-$N, and LINX/LINY coordinates for the quasilinear $\angle$N$-$N$-$O and torsion. LINX/LINY coordinates are defined in Ref. 26 and discussed in Ref. 13 for the related $HOCO^+$ cation. At each point, CCSD(T)/cc-pVXZ (where $\mathrm{X} = \mathrm{T}, \mathrm{Q}, 5$) energies are computed and extrapolated to the complete basis set limit. The same further additive corrections are included once more for core-correlation and scalar relativity to define the CcCR QFF. All electronic structure computations are performed at the CCSD(T) level of theory using the MOLPRO 2006.1 program.[29]

After a least squares fit where the sum of squared residuals is 3.4×10^{-16} a.u.^{2}, the force constants are transformed such that the gradients are identically zero. The Cartesian derivatives are computed with INTDER 2005 (Ref. 26) and, then, used to produce spectroscopic constants,[30] and vibrational frequencies[31,32] via second-order perturbation theory (VPT2) using the SPECTRO program.[33] After the force constants are transformed into Morse-cosine coordinates so that they have proper limiting behavior,[34,35] vibrational configuration interaction (VCI) theory can be employed with the the MULTIMODE program[36,37] to provide further analysis of the vibrational frequencies. The $2\nu_5 = \nu_4$ Fermi resonance is included in the SPECTRO computations for NNOH$^+$, and the $2\nu_5 = \nu_3 = \nu_4$ polyad[38] is included for NNOD$^+$. The VCI procedure utilized here has a 5-mode representation (5MR) and requires 13 contracted basis functions composed of 25 primitive functions with 16 Hermite-Gauss (HEG) quadrature points for the a' modes and 9 contracted basis functions composed of 21 primitive functions with 12 HEG points for the a'' mode.

III. RESULTS AND DISCUSSION

The force constants produced for this study are given in Table I and the anharmonic constant matrix in Table II. The equilibrium geometry is depicted in Fig. 1, and the geometric and spectroscopic constants for both NNOH$^+$ and NNOD$^+$ are listed in Table III. In this table, comparison to previous experimental work demonstrates the accuracy of the QFFs. The equilibrium geometric parameters agree well with recent high-level computations, and the given equilibrium rotational constants show improvement over previous theory. The zero-point rotational constants are in excellent agreement with experimental results for both isotopologues. The NNOH$^+$ B_{eff} computed with the zero-point rotational constants (11 198.57 MHz), where $B_{eff} = \frac{B_0+C_0}{2}$ (derived from the $K = 0$ form of the prolate top rotational energy equation given in Appendix C of Ref. 39), is also very close to its corresponding experimental value (11 192.919 4 MHz).[10]

The quartic (D) and sextic (H) centrifugal distortion constants from the Watson S-reduced Hamiltonian are equilibrium values, but they exhibit good agreement with experimental results, especially the D constants. The D_J constants for both $NNOH^+$ and $NNOD^+$, as an example, correspond to their experimental counterparts to within 3% error. The computed H-type constants are not as good as the D-type constants for $NNOH^+$, but H_{JK} is set to zero in Ref. 40 since few lines were observed. As a result of this approximation, a noticeable difference between theory and experiment is present for the H-type constants. The computed $NNOD^+$ H-type constants are much closer to the experimentally determined values than those of the standard isotopologue since these constants could be derived from the larger number of rotational lines observed for this isotopologue. The experimental D_{eff} of 7.765 kHz is determined by utilizing the A, B, C, and D_J constants given by Bogey *et al.*[40] and the same equation as above for B_{eff} from Ref. 39 with $K = 0$. The theoretical D_{eff} is computed in the same manner but with A_0, B_0, C_0, and the equilibrium D_J. It is 7.608 kHz. The difference between the two is only 0.157 kHz or just 2.02%.

Interestingly, recent attribution of lines observed in the Horsehead nebula photodissociation region (PDR) to l-C_3H^+ (Ref. 41) has been questioned[15] mainly on the grounds that the D constant derived from the observations, 7.652 kHz, is too large for it to match the CcCR D_e of l-C_3H^+ at 4.248 kHz. The $NNOH^+$ D_{eff} of 7.608 kHz is actually within 1% of the value necessary to match the D from the astronomical observations. However, the $NNOH^+$ B_{eff}, whether from the CcCR QFF computations or from experiment,[10] is more than 45 MHz lower than the necessary 11 244.947 4 MHz B. Hence, $NNOH^+$ probably cannot be the carrier of the observed rotational lines in this PDR even though the D-type constants are very close. For more discussion see Ref. 42 regarding $1\ {}^1A'$ C_3H^- as a potential carrier for the observed lines.

The fundamental vibrational frequencies are listed in Table IV. The $NNOH^+$ harmonic vibrational frequencies are in line with those computed previously[9] with the differences between the harmonic frequencies about what should be expected for the differences in the older CCDS(T)/TZ2P calculation compared to the state-of-the-art CcCR QFF reported here. The anharmonic computations performed here with VPT2 and VCI are notably consistent with one another. The VPT2/VCI difference for the ν_2 N$-$N stretching frequency, for instance, is only 0.4 cm^{-1}, and the largest difference is 2.6 cm^{-1} for the ν_4 N$-$O stretch. The ν_6 torsional frequency is also in good agreement between VPT2 and VCI with a difference of 1.9 cm^{-1}. The torsional mode has often been problematic for single-reference MULTIMODE without the reaction path coordinate formulation,[19,43,44] but the use of linear coordinates for the heavy atom bond angle in similar systems has alleviated this issue to some extent,[13,14] as it appears to do so here.

Comparison of the NNOH$^+$ CcCR QFF ν_1 O$-$H stretching frequency from either VPT2 or VCI to the the known gas phase frequency for the ν_1 O$-$H stretch is exceptional. This frequency has been observed at 3330.91 cm^{-1} in the gas phase.[6] VPT2 is 1.1 cm^{-1} higher, but VCI puts this value exactly at 3330.9 cm^{-1}. CcCR QFF accuracies within 1 cm^{-1} for known gas phase data are also reported for the O$-$H stretch of HOCO$^+$ where VCI is slightly more accurate than VPT2, as well.[13] In each case, the QFF benefits from closed-shell reference wavefunctions in the electronic structure computations, but the additional corrections for core correlation and scalar relativity also improve the accuracy of the QFF. As a result of this agreement between theory and experiment for the gas phase O$-$H stretch, comparison between the matrix-isolation ν_1 frequency[12] and the theoretical result is identical. Hence, the matrix O$-$H stretching frequency is red-shifted by 43.3 cm^{-1} away from the VCI frequency.

The NNOD$^+$ harmonic frequencies computed with the CcCR QFF are similar to those computed via RB3LYP/cc-pVTZ.[12] There are positive anharmonicities present in the two lowest frequency modes of NNOD$^+$. Similar behavior has also been noted for the other tetra-atomic cations,[13,14,45] is present in NNOH$^+$, and has been suspected in one tetra-atomic quasilinear radical, HCCO.[46] Agreement between VPT2 and VCI is actually better between the fundamental frequencies for NNOD$^+$ than it is for the standard isotopologue. The difference in the ν_3 D$-$O$-$N bend is 0.1 cm^{-1}, and the largest VPT2/VCI difference is 0.7 cm^{-1} for the ν_4 N$-$O stretch once more. No gas phase data is available for the deuterated isotopologue, but the Ne matrix experiment puts the ν_1 O$-$D stretch at 2426.3 cm^{-1}. This is 41.0 cm^{-1} lower than the VCI O$-$D stretch, similar to the 43.3 cm^{-1} red-shift for the O$-$H stretch in NNOH$^+$. These consistencies indicate that the gas phase O$-$D stretch of NNOD$^+$ should be very close to the CcCR QFF VCI frequency at 2467.3 cm^{-1}. The other fundamental vibrational frequencies should also be very close to their experimental gas phase counterparts.

The ν_3 through ν_6 fundamentals for both isotopologues fall within the spectral range covered by the EXES (SOFIA) instrument. Hence, based on the previously published infrared instrensities[7], it is expected that ν_3 or ν_4 would be most easily observed using EXES, though it would also be important to ascertain information about the target and the atmospheric conditions present for observation of a given target.

IV. CONCLUSIONS

As the sensitivity of high-resolution telescopes increases and experimental procedures improve, it will be necessary to have highly accurate reference data for new molecules of interest to both astronomers and experimentalists. $NNOH^+$ has been postulated to exist in the ISM, but a detection has yet to be reported. Only the ν_1 O$-$H stretch has been observed experimentally both in the gas and condensed phases. The $NNOD^+$ O$-$D stretch has also been observed in Ne matrix experiments. High-accuracy computational reference data for the unknown fundamental vibrational frequencies and spectroscopic constants is provided here. The gas phase ν_1 O$-$H stretch is nearly coincident with the CcCR VCI frequency at 3330.9 cm^{-1}. The experimentally known spectroscopic constants are in excellent agreement with the computational results. As a result, the highly-accurate rovibrational results reported in this study should provide the necessary reference data to assist in the detection of this molecule in the ISM and in future laboratory experiments.

V. ACKNOWLEDGEMENTS

XH and RCF were supported by Oak Ridge Associated Universities through the NASA Postdoctoral Program. The NASA/SETI Institute Cooperative Agreement NNX12AG96A further funded the work undertaken by XH. T.J.L. and X.H. gratefully acknowledge funding from NASA Grant No. 10-APRA10-0096. The CheMVP program, developed at the Center for Computational Quantum Chemistry at the University of Georgia, was used to create Fig. 1. Prof. Wesley D. Allen is thanked for helpful discussions regarding the use of the LINX/LINY coordinates for quasilinear molecules and the use of INTDER program.

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FIG. 1. NNOH$^+$ at the CcCR equilibrium geometry.

TABLE I. The NNOH$^+$ simple-internal (1-4), LINX (5) and LINY (6) CcCR QFF Quadratic, Cubic, and Quartic Force Constants (in mdyn/Å^n·rad^m).[a]

F_{11}	6.934 532	F_{431}	-0.0139	F_{1111}	303.77	F_{4432}	0.01	F_{5531}	0.15
F_{21}	0.049 406	F_{432}	-0.0520	F_{2111}	-0.89	F_{4433}	-0.16	F_{5532}	2.89
F_{22}	7.702 967	F_{433}	-0.1131	F_{2211}	-0.26	F_{4441}	1.22	F_{5533}	0.92
F_{31}	-0.120 510	F_{441}	-0.5874	F_{2221}	8.86	F_{4442}	1.53	F_{5541}	-0.10
F_{32}	0.498 582	F_{442}	-0.3618	F_{2222}	382.56	F_{4443}	0.59	F_{5542}	-0.01
F_{33}	21.257 633	F_{443}	-0.3243	F_{3111}	0.10	F_{4444}	-0.16	F_{5543}	-0.06
F_{41}	0.107 165	F_{444}	-1.3098	F_{3211}	0.35	F_{5111}	-0.01	F_{5544}	0.26
F_{42}	0.834 484	F_{511}	-0.0277	F_{3221}	-0.68	F_{5211}	-0.01	F_{5551}	0.01
F_{43}	-0.011 877	F_{521}	-0.0187	F_{3222}	2.77	F_{5221}	0.10	F_{5552}	0.73
F_{44}	1.004 344	F_{522}	-0.5501	F_{3311}	0.06	F_{5222}	0.50	F_{5553}	0.61
F_{51}	-0.010 485	F_{531}	-0.0196	F_{3321}	-0.27	F_{5311}	0.02	F_{5554}	-0.07
F_{52}	0.114 112	F_{532}	-0.3960	F_{3322}	5.38	F_{5321}	0.23	F_{5555}	3.35
F_{53}	0.124 638	F_{533}	-0.2356	F_{3331}	0.84	F_{5322}	0.90	F_{6611}	-0.02
F_{54}	0.054 977	F_{541}	-0.0348	F_{3332}	-0.51	F_{5331}	0.07	F_{6621}	-0.17
F_{55}	0.390 995	F_{542}	0.1129	F_{3333}	950.94	F_{5332}	0.65	F_{6622}	2.94
F_{66}	0.442 834	F_{543}	-0.2099	F_{4111}	-0.96	F_{5333}	-0.30	F_{6631}	0.06
F_{111}	-48.7568	F_{544}	-0.0699	F_{4211}	0.35	F_{5411}	-0.11	F_{6632}	2.88
F_{211}	0.4488	F_{551}	0.0906	F_{4221}	0.90	F_{5421}	0.07	F_{6633}	0.93
F_{221}	-1.8947	F_{552}	-0.9025	F_{4222}	-4.95	F_{5422}	-0.42	F_{6641}	0.02
F_{222}	-61.3566	F_{553}	-1.4970	F_{4311}	-0.06	F_{5431}	0.14	F_{6642}	-0.05
F_{311}	-0.0823	F_{554}	-0.0269	F_{4321}	0.36	F_{5432}	0.09	F_{6643}	-0.03
F_{321}	0.5146	F_{555}	-0.3490	F_{4322}	-0.16	F_{5433}	-0.02	F_{6644}	-0.01
F_{322}	-1.7547	F_{661}	0.0521	F_{4331}	0.06	F_{5441}	0.14	F_{6651}	0.05
F_{331}	0.0204	F_{662}	-1.1419	F_{4332}	-0.46	F_{5442}	0.19	F_{6652}	0.24
F_{332}	-0.1365	F_{663}	-1.3863	F_{4333}	0.05	F_{5443}	0.16	F_{6653}	0.18
F_{333}	-162.4211	F_{664}	-0.0417	F_{4411}	-0.50	F_{5444}	-0.12	F_{6654}	-0.01
F_{411}	-0.1491	F_{665}	-0.1206	F_{4421}	0.84	F_{5511}	-0.01	F_{6655}	1.10
F_{421}	-0.8169			F_{4422}	0.44	F_{5521}	-0.28	F_{6666}	3.41
F_{422}	-1.6277			F_{4431}	0.15	F_{5522}	2.51		

[a] 1 mdyn = 10^{-8} N; n and m are exponents corresponding to the number of units from the type of modes present in the specific force constant.

TABLE II. $NNOH^+$ and $NNOD^+$ CcCR QFF Anharmonic Constant Matrix (in cm^{-1}).[a]

	mode	1	2	3	4	5	6
$NNOH^+$	1	-86.117					
	2	-4.714	-15.321				
	3	-33.951	-3.520	-11.183			
	4	0.386	8.025	-3.919	-12.451		
	5	0.109	-10.936	1.678	-5.182*	0.549*	
	6	1.049	-11.427	1.738	1.661	40.149	-0.212
$NNOD^+$	1	-45.651					
	2	-3.218	-15.449				
	3	-15.670	-2.579	-2.374			
	4	0.942	7.089	-17.519	-9.150		
	5	0.549	-11.229	3.794[b]	-3.003*	-0.157*	
	6	0.335	-10.690	1.741	0.049	21.907	-0.038

[a] Constants marked with an asterisk (*) are effected by Fermi resonances.

[b] This term does not consider the $2\nu_5 = \nu_3$ Fermi resonance.

TABLE III. The CcCR QFF R_α Vibrationally-Averaged (Zero-Point) and Equilibrium Structures, Rotational Constants, Dipole Moment, Vibration-Rotation Interaction Constants, and S-Reduced Hamiltonian Terms of $NNOH^+$ and $NNOD^+$ with Comparison to Experiment.

	$NNOH^+$		$NNOD^+$	
	This Work	Previous	This Work	Previous
r_0(O−H)	0.998 804 Å		0.996 028 Å	
r_0(O−N)	1.276 293 Å		1.276 544 Å	
r_0(N−N)	1.105 147 Å		1.104 925 Å	
$\angle_0$(H−O−N)	108.326°		108.270°	
$\angle_0$(N−N−O)	172.110°		172.058°	
A_0	625 221.3 MHz	625 957.716 MHz[a]	348 498.3 MHz	349 107.385 MHz[a]
B_0	11 307.00 MHz	11 301.562 8 MHz[a]	10 753.40 MHz	10 747.354 03 MHz[a]
C_0	11 090.15 MHz	11 084.280 0 MHz[a]	10 412.83 MHz	10 406.948 46 MHz[a]
B_{eff}	11 198.57 MHz	11 192.919 4 MHz[b]	10 583.12 MHz	
D_{eff}	7.608 kHz	7.765 kHz[a]	15.941 kHz	
D_J	5.215 kHz	5.365 08 kHz[a]	4.411 kHz	4.548 97 kHz[a]
D_{JK}	0.697 MHz	0.725 48 MHz[a]	0.518 MHz	0.514 886 MHz[a]
D_K	223.700 MHz	242.8 MHz[c]	62.216 MHz	69.697 MHz[a]
d_1	-0.081 kHz	-0.095 0 kHz[a]	-0.123 kHz	-0.142 302 kHz[a]
d_2	-0.012 kHz	-0.017 97 kHz[a]	-0.029 kHz	-0.038 26 kHz[a]
H_J	-3.159 mHz		-24.692 mHz	
H_{JK}	0.457 Hz	0.0 Hz[d]	1.560 Hz	1.687 Hz[a]
H_{KJ}	-1.882 kHz	0.228 kHz[a]	-0.832 kHz	-0.516 0 kHz[a]
H_K	-188.103 kHz		41.399 kHz	
H_1	0.049 mHz		0.025 mHz	
H_2	0.074 mHz		0.213 mHz	
H_3	0.014 mHz		0.044 mHz	
τ_{aaaa}	-897.607 MHz		-250.957 MHz	
τ_{bbbb}	-0.022 MHz		-0.019 MHz	
τ_{cccc}	-0.020 MHz		-0.017 MHz	
τ_{aabb}	-2.370 MHz		-1.887 MHz	
τ_{aacc}	-0.461 MHz		-0.221 MHz	
τ_{bbcc}	-0.021 MHz		-0.018 MHz	
Φ_{aaa}	-189 984.848 Hz		40 568.463 Hz	
Φ_{bbb}	-0.003 Hz		-0.002 Hz	
Φ_{ccc}	-0.003 Hz		-0.002 Hz	
Φ_{aab}	290.115 Hz		102.967 Hz	
Φ_{abb}	1.855 Hz		2.440 Hz	
Φ_{aac}	-2 173.025 Hz		-932.731 Hz	
Φ_{bbc}	-0.005 Hz		-0.004 Hz	
Φ_{acc}	-1.009 Hz		-0.436 Hz	
Φ_{bcc}	-0.005 Hz		-0.003 Hz	
Φ_{abc}	0.857 Hz		2.230 Hz	
α^A 1	24 543.4 MHz		10 693.5 MHz	
α^A 2	2 175.3 MHz		452.8 MHz	
α^A 3	-27 935.3 MHz		-6 656.6 MHz	
α^A 4	-304.6 MHz		-5 933.3 MHz	
α^A 5	5 127.5 MHz		4 312.2 MHz	
α^A 6	-5 140.9 MHz		-2 188.8 MHz	
α^B 1	7.7 MHz		9.9 MHz	
α^B 2	77.4 MHz		73.1 MHz	
α^B 3	-12.9 MHz		10.2 MHz	
α^B 4	79.1 MHz		52.4 MHz	
α^B 5	-9.5 MHz		-10.4 MHz	
α^B 6	-39.9 MHz		-41.6 MHz	
α^C 1	13.6 MHz		16.9 MHz	
α^C 2	75.3 MHz		69.1 MHz	
α^C 3	3.0 MHz		-3.3 MHz	
α^C 4	81.6 MHz		86.0 MHz	
α^C 5	-29.9 MHz		-28.7 MHz	
α^C 6	-14.2 MHz		-14.3 MHz	
r_e(O−H)[e]	0.986 699 Å	0.986 0 Å[f]		
r_e(N−O)	1.271 062 Å	1.270 0 Å[f]		
r_e(N−N)	1.103 964 Å	1.104 0 Å[f]		
$\angle_e$(H−O−N)	108.290°	108.38°[f]		
$\angle_e$(N−N−O)	171.992°	172.05°[f]		
A_e	624 453.7 MHz	608 300 MHz[g]	348 838 2 MHz	
B_e	11 357.85 MHz	11 102 MHz[g]	10 800.08 MHz	
C_e	11 154.96 MHz	10 903 MHz[g]	10 475.75 MHz	
μ[h]	2.98 D	2.43 D[i]		
μ_x	2.03 D			
μ_y	2.18 D			

[a] Experimental results and derived D_{eff} from Ref. 8. [b] Experimental results from Ref. 10. [c] Experimental results from Ref. 6. [d] H_{JK} is fixed to 0.0 in Ref. 8. [e] $NNOH^+$ and $NNOD^+$ possess the same equilibrium geometries under the Born-Oppenheimer approximation.
[f] CCSD(T)/cc-pwCV5Z results from Ref. 11. [g] CCSD(T)/TZ2P results from Ref. 9. [h] The $NNOH^+$ coordinates (in Å with the center-of-mass at the origin) used to generate the CCSD(T)/aug-cc-pV5Z Born-Oppenheimer dipole moment components are: H, 1.516751, 0.826938, 0.000000; O, 1.121745, -0.077244, 0.000000; N, -0.143865, 0.040354, 0.000000; N, -1.246604, -0.011638, 0.000000. [i] CISD/DZ+P result from Ref. 7.

TABLE IV. The $NNOH^+$ and $NNOD^+$ CcCR VPT2 and VCI fundamental vibrational frequencies (in cm^{-1}) and previous theoretical and experimental results.

			Harmonic		Anharmonic		Experiment	
	Mode	Description	This Work	Previous[a]	VPT2	VCI	Ne Matrix[b]	Gas Phase[c]
$NNOH^+$	ν_1	a' O−H stretch	3522.8	3536	3332.0	3330.9	3287.6	3330.91
	ν_2	a' N−N stretch	2370.5	2314	2328.5	2328.1	–	–
	ν_3	a' H−O−N bend	1405.8	1425	1364.4	1363.8	–	–
	ν_4	a' N−O stretch	1042.0	973	1024.3	1021.7	–	–
	ν_5	a' N−N−O bend	420.5	398	436.7	434.9	–	–
	ν_6	a" torsional mode	472.2	446	486.2	484.3	–	–
$NNOD^+$	ν_1	a' O−D stretch	2566.7	2522.1	2466.9	2467.3	2426.3	–
	ν_2	a' N−N stretch	2366.6	2432.2	2325.4	2324.8	–	–
	ν_3	a' D−O−N bend	1071.3	1086.1	1051.4	1051.3	–	–
	ν_4	a' N−O stretch	1032.3	1023.6	1010.4	1009.7	–	–
	ν_5	a' N−N−O bend	404.2	430.2	410.8	410.4	–	–
	ν_6	a" torsional mode	463.4	491.8	469.1	468.6	–	–

[a] $NNOH^+$ results from CCSD(T)/TZ2P computations in Ref. 9. $NNOD^+$ results from unscaled RB3LYP/cc-pVTZ computations in Ref. 12.

[b] Ne matrix-isolation experimental data from Ref. 12.

[c] Reference 6.