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Theoretical studies for the $\text{N}_2\text{--N}_2\text{O}$ van der Waals complex: The potential energy surface, intermolecular vibrations, and rotational transition frequencies

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Theoretical studies of the potential energy surface (PES) and bound states are performed for the $\text{N}_2\text{--N}_2\text{O}$ van der Waals (vdW) complex. A four-dimensional intermolecular PES is constructed at the level of single and double excitation coupled-cluster method with a non-iterative perturbation treatment of triple excitations [CCSD(T)] with aug-cc-pVTZ basis set supplemented with bond functions. Two equivalent T-shaped global minima are located, in which the O atom of N_2O monomer is near the N_2 monomer. The intermolecular fundamental vibrational states are assigned by inspecting the orientation of the nodal surface of the wavefunctions. The calculated frequency for intermolecular disrotation mode is 23.086 cm^{-1} , which is in good agreement with the available experimental data of 22.334 cm^{-1} . A negligible tunneling splitting with the value of 4.2 MHz is determined for the ground vibrational state and the tunneling splitting increases as the increment of the vibrational frequencies. Rotational levels and transition frequencies are calculated for both isotopomers $^{14}\text{N}_2\text{--N}_2\text{O}$ and $^{15}\text{N}_2\text{--N}_2\text{O}$. The accuracy of the PES is validated by the good agreement between theoretical and experimental results for the transition frequencies and spectroscopic parameters. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933057>]

I. INTRODUCTION

It is well-known that linear triatomic molecules such as N_2O , CO_2 , and OCS form an isoelectronic species called “ CO_2 family” and have similar physical and chemical properties, especially for N_2O and CO_2 . Obviously, these two molecules have the same molecular mass and density, similar bond lengths, and similar crystal structure.^{1–3} Meanwhile, N_2O and CO_2 are the important green house gases in the atmosphere, because they have strong absorption/reemission of the radiation of the radiation emitted by the earth.^{4,5} Although the concentration of CO_2 molecule in atmosphere is far higher than that of N_2O , it has been reported that N_2O has 298 times more impact per unit mass (global warming potential, GWP) than CO_2 .⁵ Moreover, N_2O is a precursor for the production of nitrous oxides NO_x which play important roles in the depletion of stratospheric ozone.⁶ As a consequence, the molecular dynamics of the complexes concerning N_2O monomer have been the subject of much attention and extensive researches.⁷

The van der Waals (vdW) complexes consisting of a linear molecule and N_2O monomer have been extensively studied by spectroscopists and theorists. This system includes the dimers

such as a linear structure of $\text{HF--N}_2\text{O}$,^{8–10} a slipped-parallel or slipped-antiparallel structure of $(\text{N}_2\text{O})_2$,^{11–16} a nearly H-shaped structure of $\text{H}_2\text{--N}_2\text{O}$,^{17–19} and a nearly T-shaped structure of $\text{CO--N}_2\text{O}$.^{20,21} $\text{N}_2\text{--N}_2\text{O}$ is the isoelectronic dimer of $\text{CO--N}_2\text{O}$ and has particular interest in atmospheric chemistry. N_2O is one of the molecules whose atmospheric location and concentration have been continuously monitored for several decades.²² A precise characterization of the weak interactions between N_2 or O_2 and N_2O is essential for accurate calculations of the N_2 or O_2 pressure broadening coefficients of N_2O ,²² which is used to monitor the concentration of N_2O . Furthermore, it is also interesting to study the dynamics of tunneling effects of $\text{N}_2\text{--N}_2\text{O}$.

In the past decades, great efforts have been made to investigate the spectra, molecular structure, and dynamical properties for $\text{N}_2\text{--N}_2\text{O}$ complex by spectroscopists.^{23–26} In 1988, Randall *et al.*²³ first reported the rotationally resolved infrared spectrum of the $\text{N}_2\text{--N}_2\text{O}$ complex in the ν_3 asymmetric stretch region of N_2O monomer. A nearly T-shaped geometry was determined from the rotational constants and rationalized by the construction of potentials using a distributed multipole and distributed dispersion model, but no enough angular information to understand how the complex deviates from a perfect T-shaped structure. Because the hyperfine structure of $^{14}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ would be extremely complicated with four quadrupole nuclei, there is no pure rotational spectrum

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for normal isotopic complex $^{14}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ until now and precise determination of the complex structure cannot be made. In order to determine a more precise structure of this complex, Leung²⁴ investigated the pure rotational spectrum of $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ using a pulsed molecular beam Fourier transform microwave spectrometer and four possible structures of $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ were determined from the rotational constants and nuclear quadrupole coupling constants. Fortunately, $^{15}\text{N}_2$ is only 7% heavier than $^{14}\text{N}_2$, the vibrational dynamics of the two subunits can also be observed for the $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ complex. These structures are all coplanar and approximately T-shaped, with N_2 nearly perpendicular to N_2O . The angle between the intermolecular axis and $\text{N}_2/\text{N}_2\text{O}$ is $13^\circ/81^\circ$, respectively. To determine the dynamics of different vibrational modes, Zheng *et al.*²⁵ made a spectroscopic measurement for $\text{N}_2\text{--N}_2\text{O}$ in the ν_1 symmetric stretch region of N_2O monomer. The vibrational frequency of $\text{N}_2\text{--N}_2\text{O}$ in the N_2O ν_1 region has a small shift of $+0.8363\text{ cm}^{-1}$ from that of the N_2O monomer, compared with a large shift of $+2.2327\text{ cm}^{-1}$ in the ν_3 region of N_2O .¹⁸ Furthermore, a restricted two-dimensional intermolecular potential energy surface (PES) has been constructed at the level of single and double excitation coupled-cluster method with a non-iterative perturbation treatment of triple excitations [CCSD(T)] with the aug-cc-pVDZ basis set. This PES has a global minimum with a well depth of 326.64 cm^{-1} at $\theta_{\text{N}_2} = 11.0^\circ$ and $\theta_{\text{N}_2\text{O}} = 84.3^\circ$. This equilibrium structure is in agreement with the third structure determined by Leung. Recently, a new combination band involving the intermolecular in-plane bending mode was observed by Rezaei *et al.*²⁶ and the resulting intermolecular frequency is 22.334 cm^{-1} . Moreover, the fundamental band exhibits very weak a-type transitions which were not detected in Randall's work and confirms that $\text{N}_2\text{--N}_2\text{O}$ is not exactly T-shaped.²⁴

Although the above studies present important information for $\text{N}_2\text{--N}_2\text{O}$ complex, some dynamical properties are still not to be fully understood. First, due to lack of the spectroscopic information of isotopic substitution, the structure cannot be determined accurately, for example, the angle of θ_{N_2} varies from 7.1° to 28.1° using different g -Eckart angles. Second, the restricted two-dimensional intermolecular PES only confirmed one of the possible structures of $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ suggested by Leung. What is more, Rezaei *et al.* have pointed out that the intermolecular mode observed for $\text{N}_2\text{--N}_2\text{O}$ cannot be assigned due to lack of the theoretical predictions.

In the present paper, to get a better understanding of the dynamics of $\text{N}_2\text{--N}_2\text{O}$ dimer, we construct a new intermolecular PES and carry out the bound state calculations to determine the intermolecular vibrational frequencies, rotational levels, and structure for $\text{N}_2\text{--N}_2\text{O}$ dimer. This work will provide unambiguous answers to the questions mentioned above and are useful for the further investigation of the dynamics for $\text{N}_2\text{--N}_2\text{O}$ dimer, clusters, and N_2O in solid N_2 .²⁷

The remainder of this paper is organized as follows. Section II gives a detailed description for *ab initio* PES and bound state calculations. The results including the PES, bound state energy levels, intermolecular vibrational frequencies, and rotational transitions are presented in Section III. In Section IV, we conclude the paper.

II. COMPUTATIONAL DETAILS

A. *Ab initio* calculations of intermolecular potential energy

In this work, the N_2 and N_2O monomers are assumed to be the linear rigid rotors and are fixed at their equilibrium structures: $r(\text{N--N}) = 1.0977\text{ \AA}$ for N_2 ,²⁸ $r(\text{N--N}) = 1.1273\text{ \AA}$, and $r(\text{N--O}) = 1.1851\text{ \AA}$ for N_2O .²⁹ Accordingly, the intermolecular PES of $\text{N}_2\text{--N}_2\text{O}$ dimer can be described by four Jacobi coordinates ($R, \theta_1, \theta_2, \varphi$) as shown in Fig. 1. R is the vector connecting the centers of mass of the N_2 and N_2O monomers. The molecular axis of the N_2 molecule is denoted by the vector r_1 , and that of the N_2O molecule is the vector r_2 pointing from the N-atom to the O-atom. The angles θ_1 and θ_2 are the enclosed angles of $R\text{--}r_1$ and $R\text{--}r_2$, respectively. The dihedral angle φ is the torsional angle used to describe the out-of-plane vibration.

The *ab initio* potential energy grids are chosen as follows: The grids for R include 18 points ranging from $2.0\text{ \AA}$ to $9.0\text{ \AA}$. The angles θ_1 and θ_2 vary from 0° to 180° in steps of 15° and φ varies from 0° to 360° in steps of 30° . Taking account of symmetry, 11 466 geometries are finally selected, which covered the short-range repulsive region, the van der Waals well, and the long-range attractive part of the PES. The global four-dimensional intermolecular PES is constructed by executing a series of one-dimensional interpolation with the Lagrange polynomial formula. The potential of a specific geometry, $U(R', \theta'_1, \theta'_2, \varphi')$, is interpolated from *ab initio* potential energy grids. $U(R', \{\theta_1\}, \{\theta_2\}, \{\varphi\})$ which contain $N_R \times N_{\theta_1} \times N_{\theta_2} \times N_\varphi$ geometries. This 4D interpolation calculation is finished in four steps. Each step interpolates on one coordinate and keeps other coordinates fixed. For example, in step 1, $N_{\theta_1} \times N_{\theta_2} \times N_\varphi$ one-dimensional interpolations are carried out for R and a 3-dimensional potential energy grid $U(R', \{\theta_1\}, \{\theta_2\}, \{\varphi\})$ is obtained. The whole procedure is expressed as

$$\begin{aligned} U(\{R\}, \{\theta_1\}, \{\theta_2\}, \{\varphi\}) \\ \rightarrow U(R', \{\theta_1\}, \{\theta_2\}, \{\varphi\}) \rightarrow U(R', \theta'_1, \{\theta_2\}, \{\varphi\}) \\ \rightarrow U(R', \theta'_1, \theta'_2, \{\varphi\}) \rightarrow U(R', \theta'_1, \theta'_2, \varphi'). \end{aligned} \quad (1)$$

The interpolated energies are independent of the order of these one-dimensional interpolations.³⁰ In order to test the accuracy of this interpolated PES, *ab initio* calculations of interaction energy are carried out for other 1362 geometries. By comparing the interpolated potential energy with *ab initio* calculated values, the root mean square deviation (RMSD) of the validate set is 0.774 cm^{-1} . For the geometries with negative interaction

FIG. 1. Jacobi coordinates for the $\text{N}_2\text{--N}_2\text{O}$ van der Waals complex.

energy, the RMSD is 0.313 cm^{-1} , indicating that this interpolated PES shows high accuracy.

The intermolecular potential energy for each geometry was calculated using the supermolecular method at the level of single and double excitation coupled-cluster method with a non-iterative perturbation treatment of triple excitations [CCSD(T)].³¹ The aug-cc-pVTZ basis set of Woon and Dunning³² was used in the current work. The bond functions (3s3p2d1f) (for 3s and 3p, $\alpha = 0.9, 0.3, 0.1$; for 2d, $\alpha = 0.6, 0.2$; for f, $\alpha = 0.3$)³³ were placed at the middle point of the intermolecular distance R . The full counterpoise procedure of Boys and Bernardi³⁴ was employed to correct the basis set superposition error (BSSE). All the calculations were carried out using the MOLPRO 2010 software package.³⁵

B. Bound state calculations

Within the rigid rotor approximation for the monomer, the Hamiltonian of the $\text{N}_2\text{--N}_2\text{O}$ dimer in Jacobi coordinates can be written as

$$H = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu R^2} + B_{\text{N}_2} \hat{j}_1^2 + B_{\text{N}_2\text{O}} \hat{j}_2^2 + U(R, \theta_1, \theta_2, \varphi). \quad (2)$$

Here, μ is the reduced mass of the complex. $\hat{J}$ is the total angular momentum and $\hat{j}_{12} = \hat{j}_1 + \hat{j}_2$, while $\hat{j}_1$ and $\hat{j}_2$ are the angular momenta of the N_2 and N_2O monomers. B_{N_2} is the rotational constant of N_2 molecule with the value of $1.989\,574 \text{ cm}^{-1}$ for $^{14}\text{N}_2$ and $1.857\,624 \text{ cm}^{-1}$ for $^{15}\text{N}_2$ in the ground vibrational state.²⁸ $B_{\text{N}_2\text{O}}$ is the rotational constant of $^{14}\text{N}_2\text{O}$ with the value of $0.419\,011 \text{ cm}^{-1}$.²⁹

The wavefunction of the system can be expanded as a linear combination of products of the radial and angular basis functions and written as follows:

$$\psi = \sum_i \sum_K \sum_{j_1 j_2 j_{12}} c_{j_1 j_2 j_{12}}^{iK} \varphi(R) Y_{j_1 j_2 j_{12}}^{JMK\varepsilon}, \quad (3)$$

where $\varphi_i(R)$ are the radial basis functions describing the intermolecular stretch and are chosen as sine functions in this work. ε is the index of the space-inverse parity of the system, and $Y_{j_1 j_2 j_{12}}^{JMK\varepsilon}$ is the total symmetry-adapted angular basis function, which has the following explicit form:

$$Y_{j_1 j_2 j_{12}}^{JMK\varepsilon} = \frac{1}{\sqrt{2(1 + \delta_{K0})}} \times [D_{MK}^{*J} Y_{j_1 j_2}^{j_{12}K} + \varepsilon(-1)^{J+j_{12}+j_1+j_2} D_{M-K}^{*J} Y_{j_1 j_2}^{j_{12}-K}]. \quad (4)$$

The total angular basis function is expressed in a body-fixed frame, where D_{MK}^J is a Wigner rotation matrix which is used to describe the overall rotation of the $\text{N}_2\text{--N}_2\text{O}$ system and $Y_{j_1 j_2}^{j_{12}K}$ takes the form

$$Y_{j_1 j_2}^{j_{12}K}(\theta_1, \theta_2, \varphi) = \sum_m \langle j_1 m_1 j_2 K - m | j_{12} K \rangle y_{j_1 m_1}(\theta_1, \varphi) y_{j_2 K-m_1}(\theta_2, 0), \quad (5)$$

where $\langle j_1 m_1 j_2 K - m | j_{12} K \rangle$ is a Clebsch-Gordan coefficient and y_{jm} is spherical function describing the rotations of the two monomers. Further details of the calculation of the Hamiltonian matrix elements can be found elsewhere.³⁶

The bound state calculation program is message passing interface (MPI) parallelized and the PARPACK software package was applied to solve the eigenvalues and eigenfunctions of the bound states.³⁷ The details of bound state calculation method have been described in our previous works.³⁰ Because of the symmetry of the N_2 molecule, the eigenfunctions of the $\text{N}_2\text{--N}_2\text{O}$ complex could be labeled with indexes (ε, p), where p is the parity of j_1 . All eigenfunctions are divided into 4 symmetry blocks: (+1, odd), (+1, even), (−1, odd), and (−1, even). Each block can be solved separately. To compare with experimental microwave spectrum and infrared combination differences for $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ and $^{14}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ complexes, the rovibrational bound states were calculated with the total angular momentum up to $J_{\text{tot}} = 5$ for both complexes. To obtain eigenvalues converged to 0.001 cm^{-1} , 80 sine basis functions were used for R in the range from 4.0 bohrs to 12.0 bohrs, and the size of rotational basis functions is controlled by setting $j_{1\text{max}} = j_{2\text{max}} = 45$ and also depends on both the values of J_{tot} and the parity ε .

III. RESULTS AND DISCUSSION

A. *Ab initio* potential energy surface

Three contour plots of PES are presented in Figure 2 using the Jacobi coordinates $\theta_1\text{--}\theta_2$, $R\text{--}\theta_1$, and $R\text{--}\theta_2$, respectively. Some geometries and energies of the global minima (A, A') and the saddle point (T_s) on this *ab initio* PES are listed in Table I, as well as the previous results for comparison. A and A' are two equivalent global minima with a well depth of 334.714 cm^{-1} at the configurations of $R = 3.66 \text{ \AA}$, $\theta_1 = 171.0^\circ$, $\theta_2 = 95.0^\circ$, $\varphi = 0.0^\circ$ and $R = 3.66 \text{ \AA}$, $\theta_1 = 9.0^\circ$, $\theta_2 = 95.0^\circ$, $\varphi = 180.0^\circ$. Two global minima on this potential are connected via a saddle point (T_s). This saddle point (T_s) has a distorted tetrahedral geometry with the barrier height of 142.606 cm^{-1} at the configuration of $R = 3.35 \text{ \AA}$, $\theta_1 = 90.0^\circ$, $\theta_2 = 95.0^\circ$, $\varphi = 90.0^\circ$, which undergoes a similar geometry with that of $\text{H}_2\text{--N}_2\text{O}$.¹⁸ The previous two-dimensional intermolecular PES²⁵ with the intermolecular distance and dihedral angle fixed at $R = 3.6926 \text{ \AA}$ and $\varphi = 0.0^\circ$ has one global minimum and one saddle point, which correspond to the global minimum (A) and the saddle point (T_s) in this work. As seen in Table I, the global minimum of the previous potential is in good agreement with present results, but the saddle point (T_s) shows prominent

FIG. 2. Contour plots of the intermolecular potential energy surface for the ground state of $\text{N}_2\text{-N}_2\text{O}$ complex, R in angstrom, and θ_1 , θ_2 , and φ in degree.

TABLE I. Important geometries and their corresponding energies on the PES.

	Type	R (angstrom)	θ_1 (degree)	θ_2 (degree)	Φ (degree)	Energy (cm^{-1})
This work	A	3.66	171.0	95.0	0.0	-334.714
	A'	3.66	9.0	95.0	180.0	-334.714
	T_s	3.35	90.0	95.0	90.0	-192.106
Previous work ^a	A'	3.69	169.0	95.7	0.0	-326.64
	T_s	3.69	82.6	87.8	0.0	-122.03
	MIN_1	3.69	0.0	90.0	90.0	-321.24
$\text{N}_2\text{-CO}_2^b$	MIN_2	4.48	90.0	0.0	90.0	-158.90
	T_{S1}	3.40	90.0	90.0	90.0	-163.58
	T_{S2}	5.25	0.0	0.0	90.0	-30.56

^aThese values given in Ref. 25.

^bThese values given in Ref. 38.

TABLE II. The intermolecular vibrational levels for $\text{N}_2\text{-N}_2\text{O}$ complex (in cm^{-1}).

No. of root	(1, even)	(1, odd)	(-1, even)	(-1, odd)
1	-239.416 21	-239.415 93	-208.942 21	-208.953 55
2	-216.330 10	-216.329 32	-185.727 39	-185.714 57
3	-194.155 39	-194.143 02	-166.532 91	-167.334 18
4	-191.684 19	-191.669 48	-163.341 05	-163.372 08
5	-180.669 16	-180.447 49	-153.562 07	-155.337 37
6	-177.223 28	-177.239 56	-150.972 63	-150.647 25
7	-172.748 57	-172.774 68	-144.093 81	-143.926 43
8	-166.569 73	-166.565 41	-140.434 16	-140.613 66
9	-159.628 15	-159.530 21	-133.076 42	-136.801 38
10	-157.140 04	-157.265 27	-131.491 65	-132.724 22
11	-152.946 12	-152.696 45	-126.320 43	-130.041 14
12	-150.217 89	-149.307 16	-124.493 77	-125.846 99
13	-148.694 54	-145.559 93	-121.454 08	-124.968 82
14	-144.011 56	-143.137 15	-121.354 58	-119.195 41
15	-142.738 98	-142.212 02	-116.563 10	-118.051 17
16	-139.196 02	-139.419 36	-116.247 74	-116.795 12
17	-137.285 01	-136.288 53	-111.463 08	-114.686 75
18	-134.290 76	-134.211 94	-109.778 22	-113.448 68
19	-131.465 92	-130.591 95	-107.814 05	-110.492 29
20	-129.184 52	-128.651 28	-105.878 76	-109.688 37
21	-127.870 68	-127.463 60	-103.250 90	-106.872 63
22	-126.855 72	-126.268 63	-103.002 28	-106.176 94
23	-125.267 07	-124.613 91	-102.190 27	-104.108 27
24	-124.573 38	-124.069 77	-100.516 18	-103.746 64
25	-123.641 86	-121.147 38	-99.935 29	-101.739 44

differences between the two PESs, especially for the barrier height.

Very recently, Frisch *et al.*³⁸ reported an intermolecular PES of $\text{N}_2\text{-CO}_2$ complex, which was constructed at the CCSD(T)-F12a/aug-cc-pVTZ level. Two local minima and two saddle points are found on the potential and the corresponding parameters are also listed in Table I. Similar to our results, the global minimum also corresponds to two equivalent T-shaped structure and the saddle point T_{S1} connects the two global wells. Furthermore, Min_2 is located at $R = 4.48 \text{ \AA}$, $\theta_1 = 90.0^\circ$, $\theta_2 = 0.0^\circ$, and $\varphi = 90.0^\circ$ and also corresponds to a T-shape structure where one O atom of CO_2 molecule points towards the center of mass of N_2 . The similar local minimum cannot be found for $\text{N}_2\text{-N}_2\text{O}$ complex and also for the similar saddle point (T_{S2}), which connects the two equivalent minima Min_2 .

B. Intermolecular vibrational states

Compared with our previous works of $\text{CO}_2\text{-N}_2\text{O}$ dimer,³⁰ the bound states of intermolecular vibrational modes for $\text{N}_2\text{-N}_2\text{O}$ are assigned much more straightforwardly due to only two equivalent wells. The calculated values for the first 50 roots were listed in Table II. Ordinarily, the first lower vibrational states are of interest and might be observed experimentally. Our calculation is to obtain the vibrational excited states corresponding to four fundamental intermolecular vibrational modes for the nearly T-shaped

TABLE III. The intermolecular vibrational energy levels, frequency, splitting (in cm^{-1}), and assignments (n_{dis} , n_{tor} , n_r , n_{co}). Block is labeled by (ε, j_1) , where ε is the index of the space-inverse parity of the system and j_1 is the angular momentum for N_2 monomer.

Assignment	Energy	Splitting	Frequency	Expt. ^a	(ε, j_1)	No. in block
Ground state (0,0,0,0)	-239.416 21	0.000 25	0.000	...	(1, even)	1
	-239.415 96				(1, odd)	1
Disrotation (1,0,0,0)	-216.330 10	0.000 78	23.085 86	22.334(1)	(1, even)	2
	-216.329 32		23.086 89		(1, odd)	2
Torsion (0,1,0,0)	-208.953 55	0.011 34	30.462 66	...	(-1, odd)	1
	-208.942 21		30.473 75		(-1, even)	1
Dissociation (0,0,1,0)	-191.684 19	0.014 71	47.732 02	...	(1, even)	4
	-191.669 48		47.746 73		(1, odd)	4

^aThis value given in Ref. 26.

FIG. 3. The θ_1 - θ_2 contour plots of the wavefunctions and the schematic diagrams of corresponding vibrational modes. (a) Ground vibrational state. (b) Disrotation vibrational state.

FIG. 4. The θ_1 - θ_2 and R - φ contour plots of the torsion vibrational state wavefunction.

structure. Similar to the $\text{CO}_2\text{-N}_2\text{O}$ dimer, the first four fundamental vibrational states are labeled as $(n_{\text{dis}}, n_{\text{tor}}, n_r, n_{\text{co}})$, which correspond to the in-plane disrotation (or “in-plane geared bending”), out-of-plane torsion, dissociation (or vdW stretching), and in-plane conrotation (or in-plane antigeared bending) modes, respectively. Two of them can be assigned unambiguously via the analysis of wavefunctions and the 4th root in (1, even) and (1, odd) blocks is tentatively assigned to the dissociation vibrational mode. The energy levels of the successfully assigned vibrational states are listed in Table III, including the available experimental values for comparison.

The intermolecular vibrational excited states could be identified from their wavefunction plots in discrete variable representation (DVR) by counting the number of nodal points or nodal surfaces. With the help of the contour plots presented in Figure 3 and Figure 4, the disrotation and torsion excited states are assigned unambiguously. The disrotation and dissociation vibrational states are assigned to be the 2nd and the 4th roots in the (+1, even) and (+1, odd), but the torsion mode is assigned to be the 2nd root in the (-1, odd) and (-1, even).

Following the contour plot presented in Figure 5, we tentatively assigned this excited vibrational state to the dissociation vibrational mode. As seen the portion (a) in Figure 5,

FIG. 5. The R - θ_1 , θ_2 - φ , θ_1 - θ_2 , and R - φ contour plots of the wavefunctions and the schematic diagrams of stretching mode.

the R - θ_1 contour plot shows that such vibrational state is the stretching mode exactly; however, it should be noted that this node also undergoes a nonplanar torsional vibration from the φ - θ_2 contour plot. A reasonable explanation could be given by the interchange of N nuclei between two equivalent global minima upon stretching vibrational excitation. For the conrotation vibrational state, the *ab initio* calculated value with G09 Software package³⁹ for this vibrational mode is 85.51 cm⁻¹. Therefore, we performed the bound state calculations with

the roots up to 50 and the vibrational frequency more than 120 cm⁻¹ for the even and odd parity blocks, but the typical contour plot cannot be found for the conrotation excited state yet. In our previous work, the conrotation excited state of the CO₂-N₂O²⁵ T-shape isomer is also not assigned because the wavefunction is mixed with another vibrational state at the higher frequency region, so we believe that there is a similar dynamical characteristic for the nearly T-shaped structure of N₂-N₂O complex.

TABLE IV. Tunneling splitting of the rotational transitions with $J \leq 5$ and $K_a \leq 1$ for ¹⁵N₂-¹⁴N₂O.

J	K_a	K_c	Internal motion ground state (MHz) ^a	Internal motion excited state (MHz) ^a	Splitting (MHz)
1	0	1	3 746.67	3 743.98	2.70
2	0	2	11 236.09	11 226.56	9.53
1	1	1	14 520.07	14 521.08	-1.01
1	1	0	14 808.26	14 807.13	1.14
2	1	2	21 727.01	21 724.76	2.24
3	0	3	22 460.43	22 437.03	23.40
2	1	1	22 591.58	22 582.99	8.58
3	1	3	32 538.33	32 527.34	10.99
3	1	2	34 267.40	34 243.98	23.41
4	0	4	37 408.01	37 359.38	48.63
4	1	4	46 955.25	46 925.35	29.90
4	1	3	49 836.64	49 786.63	50.02
5	0	5	56 063.55	55 972.52	91.03
5	1	5	64 979.52	64 914.37	65.15
5	1	4	69 300.38	69 206.12	94.26

^aThese levels calculated from the rotational constants given in Ref. 24.

Recently, Rezaei *et al.* reported a new combination band for $\text{N}_2\text{-N}_2\text{O}$ and the intermolecular frequency is determined to be $22.334(1) \text{ cm}^{-1}$. The spectral result showed that this band displays the nature of the intermolecular in-plane bending mode. The first vibrational mode assigned from the wavefunction analysis is the disrotation (in-plane geared bending) with the vibrational mode of 23.086 cm^{-1} . This result is in good agreement with the experimental determination and the deviation is only 0.75 cm^{-1} . The good agreement between the theoretical and experimental values shows the ability of this *ab initio* PES to predict the bound states. Therefore, our predicted frequency of the torsion vibrational mode is about 30.5 cm^{-1} , which is helpful for spectroscopists to observe the related band of $\text{N}_2\text{-N}_2\text{O}$ dimer experimentally.

Since there are two equivalent structures for the $\text{N}_2\text{-N}_2\text{O}$ complex, it is interesting to discuss the quantum tunneling effect between them. As presented above, the two equivalent global minima are connected by a saddle point corresponding to a distorted tetrahedral structure with the bar-

rier of 142.60 cm^{-1} . Because of the high barrier, quantum tunneling is difficult to occur via the rotation of N_2 molecule around intermolecular axis. Therefore, the vibrational ground state is double splitting with the energy of $-239.416\,21$ and $-239.415\,96 \text{ cm}^{-1}$, respectively. The corresponding zero point energy is 95.298 cm^{-1} . The value of tunneling splitting is only $0.000\,25 \text{ cm}^{-1}$ for $^{14}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ (about 7.5 MHz). The tunneling effect has been well illustrated by the microwave results for $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$,²⁵ but the accurate tunneling splitting was not given by Leung. Fortunately, we can estimate the vibrational splitting from the given rotational constants of two internal motion states. As seen in Table IV, the values of rotational splitting observed from experiment vary from 1 MHz to 95 MHz for $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$. Since the splitting of vibrational state should be much larger than that of rotational state, the effective vibrational splitting for $\text{N}_2\text{-N}_2\text{O}$ must be more than 95 MHz . It is well-known that the vibrational tunneling splitting is calculated according to the barrier height on the PES. In this work, the vibrational splitting for $^{15}\text{N}_2\text{-N}_2\text{O}$ is calculated to be

TABLE V. Calculated rotational energy levels (in cm^{-1}) for $\text{N}_2\text{-N}_2\text{O}$ complex.

$^{14}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$				$^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$			
Levels	Energies	Levels	Energies	Levels	Energies	Levels	Energies
0 ₀₀	-239.416 21	4 ₁₃	-237.711 09	0 ₀₀	-240.869 40	4 ₁₃	-239.588 55
	-239.415 96		-237.710 86		-240.869 26		-239.588 41
1 ₀₁	-239.286 93	4 ₂₃	-236.675 54	1 ₀₁	-240.518 97	4 ₂₃	-238.542 56
	-239.286 68		-236.675 31		-240.518 82		-238.542 42
1 ₁₁	-238.929 77	4 ₂₂	-236.672 33	1 ₁₁	-240.490 64	4 ₂₂	-238.539 83
	-238.929 52		-236.672 10		-240.490 49		-238.539 69
1 ₁₀	-238.919 56	4 ₃₂	-234.864 14	1 ₁₀	-239.411 43	4 ₃₂	-236.720 18
	-238.919 31		-234.863 91		-239.411 29		-236.720 05
2 ₀₂	-239.028 61	4 ₃₁	-234.864 12	2 ₀₂	-239.411 25	4 ₃₁	-236.720 17
	-239.028 35		-234.863 89		-239.411 11		-236.720 03
2 ₁₂	-238.681 49	4 ₄₁	-232.328 69	2 ₁₂	-241.242 00	4 ₄₁	-234.169 25
	-238.681 24		-232.328 46		-241.241 85		-234.169 11
2 ₁₁	-238.650 86	4 ₄₀	-232.328 69	2 ₁₁	-241.117 74	4 ₄₀	-234.169 25
	-238.650 62		-232.328 46		-241.117 59		-234.169 11
2 ₂₁	-237.579 43	5 ₀₅	-237.484 86	2 ₂₁	-240.757 99	5 ₀₅	-239.384 74
	-237.579 18		-237.484 63		-240.757 84		-239.384 60
2 ₂₀	-237.579 21	5 ₁₅	-237.193 47	2 ₂₀	-240.748 55	5 ₁₅	-239.086 26
	-237.578 97		-237.193 24		-240.748 40		-239.086 12
3 ₀₃	-238.641 66	5 ₁₄	-237.040 49	3 ₀₃	-240.497 38	5 ₁₄	-238.944 77
	-238.641 42		-237.040 27		-240.497 24		-238.944 64
3 ₁₃	-238.309 22	5 ₂₄	-236.030 34	3 ₁₃	-240.160 56	5 ₂₄	-237.922 31
	-238.308 97		-236.030 12		-240.160 41		-237.922 31
3 ₁₂	-238.247 97	5 ₂₃	-236.022 88	3 ₁₂	-240.103 92	5 ₂₃	-237.915 96
	-238.247 73		-236.022 66		-240.103 78		-237.915 83
3 ₂₂	-237.191 96	5 ₃₃	-234.218 46	3 ₂₂	-239.038 98	5 ₃₃	-236.099 58
	-237.191 72		-234.218 24		-239.038 84		-236.099 52
3 ₂₁	-237.190 89	5 ₃₂	-234.218 38	3 ₂₁	-239.038 07	5 ₃₂	-236.099 44
	-237.190 65		-234.218 16		-239.037 93		-236.099 38
3 ₃₁	-235.380 59	5 ₄₂	-231.684 22	3 ₃₁	-237.216 59	5 ₄₂	-233.549 74
	-235.380 35		-231.684 01		-237.216 45		-233.549 61
3 ₃₀	-235.380 58	5 ₄₁	-231.684 22	3 ₃₀	-237.216 59	5 ₄₁	-233.549 74
	-235.380 35		-231.684 00		-237.216 45		-233.549 61
4 ₀₄	-238.126 79	5 ₅₁	-228.424 04	4 ₀₄	-240.002 24	5 ₅₁	-230.269 70
	-238.126 56		-228.423 82		-240.002 10		-230.269 57
4 ₁₄	-237.813 13	5 ₅₀	-228.424 04	4 ₁₄	-239.682 92	5 ₅₀	-230.269 70
	-237.812 90		-228.423 82		-239.682 78		-230.269 57

TABLE VI. Calculated transition frequencies (in cm^{-1}) of $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ complex. The experimental data are calculated by using the molecular data given in Ref. 24.

J'	K_a'	K_c'	J''	K_a''	K_c''	Ground internal rotational state			Excited internal rotational state		
						Expt.	Cal.	Expt.–Cal.	Expt.	Cal.	Expt.–Cal.
1	1	0	1	1	1	0.009 61	0.009 44	0.000 17	0.009 54	0.009 44	0.000 10
1	1	1	2	0	2	0.109 70	0.111 41	–0.001 71	0.109 86	0.111 42	–0.001 56
1	0	1	0	0	0	0.124 96	0.124 26	0.000 70	0.124 88	0.124 26	0.000 62
1	1	0	1	0	1	0.368 98	0.369 19	–0.000 22	0.368 97	0.369 19	–0.000 22
1	1	1	0	0	0	0.484 32	0.484 01	0.000 31	0.484 32	0.484 01	0.000 31
2	1	1	2	1	2	0.028 84	0.028 33	0.000 51	0.028 62	0.028 33	0.000 29
2	1	2	1	1	1	0.240 24	0.239 02	0.001 22	0.240 17	0.239 02	0.001 15
2	0	2	1	0	1	0.249 66	0.248 34	0.001 32	0.249 57	0.248 33	0.001 24
2	1	1	1	1	0	0.259 47	0.257 91	0.001 56	0.259 24	0.257 91	0.001 33
2	1	1	2	0	2	0.378 78	0.378 76	0.000 02	0.378 65	0.378 77	–0.000 12
2	1	2	1	0	1	0.599 60	0.598 77	0.000 83	0.599 60	0.598 77	0.000 83
2	2	1	3	1	2	0.689 16	0.692 49	–0.003 33	0.689 42	0.692 49	–0.003 07
2	2	0	3	1	3	0.747 02	0.749 31	–0.002 29	0.746 84	0.749 30	–0.002 47
2	2	0	2	1	1	1.078 28	1.079 39	–0.001 11	1.078 33	1.079 38	–0.001 05
2	2	1	2	1	2	1.106 93	1.107 54	–0.000 62	1.106 76	1.107 53	–0.000 77
2	2	1	1	1	0	1.337 55	1.337 12	0.000 43	1.337 39	1.337 11	0.000 28
2	2	0	1	1	1	1.347 35	1.346 74	0.000 61	1.347 12	1.346 73	0.000 39
2	2	1	2	0	2	1.456 86	1.457 97	–0.001 11	1.456 79	1.457 97	–0.001 18
2	2	0	1	0	1	1.706 72	1.706 49	0.000 23	1.706 55	1.706 48	0.000 07
3	0	3	2	1	2	0.023 93	0.021 59	0.002 34	0.023 84	0.021 58	0.002 26
3	1	2	3	1	3	0.057 68	0.056 64	0.001 03	0.057 23	0.056 63	0.000 60
3	1	3	2	1	2	0.360 09	0.358 41	0.001 68	0.360 12	0.358 41	0.001 71
3	0	3	2	0	2	0.373 87	0.372 02	0.001 85	0.373 87	0.372 02	0.001 85
3	2	2	2	2	1	0.374 63	0.372 45	0.002 18	0.374 30	0.372 45	0.001 85
3	2	1	2	2	0	0.375 39	0.373 18	0.002 21	0.375 05	0.373 18	0.001 86
3	1	2	2	1	1	0.388 93	0.386 72	0.002 21	0.388 72	0.386 71	0.002 01
3	1	2	3	0	3	0.393 84	0.393 46	0.000 38	0.393 51	0.393 46	0.000 04
3	2	2	4	1	3	0.545 72	0.549 57	–0.003 85	0.545 70	0.549 57	–0.003 87
3	2	1	4	1	4	0.642 78	0.644 85	–0.002 07	0.641 97	0.644 85	–0.002 88
3	1	3	2	0	2	0.710 03	0.708 84	0.001 19	0.710 14	0.708 85	0.001 29
3	2	1	4	0	4	0.961 25	0.964 17	–0.002 92	0.960 58	0.964 17	–0.003 59
3	2	1	3	1	2	1.064 74	1.065 85	–0.001 11	1.064 65	1.065 85	–0.001 20
3	2	2	3	1	3	1.121 46	1.121 58	–0.000 12	1.120 95	1.121 57	–0.000 62
3	2	2	2	1	1	1.452 72	1.451 66	0.001 06	1.452 45	1.451 65	0.000 80
3	2	2	3	0	3	1.457 63	1.458 40	–0.000 77	1.457 23	1.458 40	–0.001 17
3	2	1	2	1	2	1.482 51	1.480 90	0.001 61	1.481 99	1.480 89	0.001 10
4	1	3	4	1	4	0.096 11	0.094 37	0.001 74	0.095 35	0.094 37	0.000 98
4	0	4	3	1	3	0.161 17	0.158 32	0.002 85	0.161 30	0.158 31	0.002 99
4	2	3	5	1	4	0.398 04	0.402 21	–0.004 17	0.397 50	0.402 22	–0.004 72
4	1	3	4	0	4	0.414 58	0.413 69	0.000 88	0.413 95	0.413 69	0.000 26
4	1	4	3	1	3	0.479 63	0.477 64	0.001 99	0.479 91	0.477 63	0.002 28
4	0	4	3	0	3	0.497 33	0.495 14	0.002 19	0.497 58	0.495 14	0.002 44
4	2	3	3	2	2	0.499 08	0.496 42	0.002 66	0.498 89	0.496 42	0.002 47
4	2	2	3	2	1	0.500 98	0.498 24	0.002 74	0.500 74	0.498 10	0.002 64
4	1	3	3	1	2	0.518 07	0.515 37	0.002 70	0.518 03	0.515 37	0.002 66
4	2	2	5	1	5	0.545 01	0.546 43	–0.001 42	0.543 22	0.546 43	–0.003 21
4	1	4	3	0	3	0.815 79	0.814 46	0.001 33	0.816 19	0.814 46	0.001 73
4	2	2	4	1	3	1.047 65	1.048 72	–0.001 07	1.047 37	1.048 72	–0.001 35
4	2	3	4	1	4	1.140 91	1.140 36	0.000 55	1.139 94	1.140 36	–0.000 42
4	2	3	4	0	4	1.459 38	1.459 68	–0.000 30	1.458 54	1.459 68	–0.001 14
4	2	3	3	1	2	1.562 87	1.561 36	0.001 51	1.562 62	1.561 36	0.001 26
4	2	2	3	1	3	1.623 39	1.620 73	0.002 66	1.622 62	1.620 72	0.001 90
5	1	4	5	1	5	0.144 13	0.141 49	0.002 64	0.142 94	0.141 48	0.001 46
5	0	5	4	1	4	0.301 35	0.298 18	0.003 17	0.301 91	0.298 18	0.003 73
5	1	4	5	0	5	0.441 53	0.439 97	0.001 56	0.440 53	0.439 96	0.000 57
5	1	5	4	1	4	0.598 75	0.596 66	0.002 09	0.599 50	0.596 66	0.002 83
5	0	5	4	0	4	0.619 81	0.617 50	0.002 31	0.620 52	0.617 50	0.003 02
5	2	4	4	2	3	0.623 17	0.620 25	0.002 92	0.623 32	0.620 11	0.003 21

TABLE VI. (Continued.)

J'	K_a'	K_c'	J''	K_a''	K_c''	Ground internal rotational state			Excited internal rotational state		
						Expt.	Cal.	Expt.-Cal.	Expt.	Cal.	Expt.-Cal.
5	2	3	4	2	2	0.626 95	0.623 87	0.003 08	0.627 01	0.623 86	0.003 15
5	1	4	4	1	3	0.646 77	0.643 78	0.002 99	0.647 09	0.643 77	0.003 32
5	1	5	4	0	4	0.917 21	0.915 98	0.001 23	0.918 10	0.915 98	0.002 12
5	2	3	5	1	4	1.027 84	1.028 81	-0.000 97	1.027 28	1.028 81	-0.001 53
5	2	4	5	1	5	1.165 33	1.163 95	0.001 38	1.163 76	1.163 81	-0.000 05
5	2	4	5	0	5	1.462 74	1.462 43	0.000 31	1.461 35	1.462 29	-0.000 94
5	2	4	4	1	3	1.667 97	1.666 24	0.001 73	1.667 91	1.666 10	0.001 81
5	2	3	4	1	4	1.770 71	1.766 96	0.003 75	1.769 72	1.766 95	0.002 77
5	2	3	4	0	4	2.089 18	2.086 28	0.002 90	2.088 33	2.086 27	0.002 06
RMSD							0.001 94			0.001 99	

only 4.2 MHz, which is significantly smaller than the estimated value, indicating that the barrier height determined in this work is much larger than the real barrier between the two equivalent structures. Normally, the tunneling effects increase as the increment of the fundamental vibrational frequencies. As seen in Table III, the tunneling splitting became significant with the values more than 0.01 cm⁻¹ for torsion and dissociation, we believe that tunneling effect is much larger for conrotation excited state, and it is also an important factor to prevent us from assigning this vibrational mode unambiguously.

The average structural parameters $\langle R \rangle$, $\langle \theta_1 \rangle$, and $\langle \theta_2 \rangle$ for a particular vibrational state could be determined from the wavefunctions as follows:^{40,41}

$$\left\langle \frac{1}{R^2} \right\rangle \approx \frac{1}{\langle R_2 \rangle} \quad \text{and} \quad P_2(\cos \langle \theta \rangle) \approx \langle P_2(\cos \theta) \rangle, \quad (6)$$

where θ denotes angles θ_1 or θ_2 . P_2 is the second order Legendre function and $\langle P_2(\cos \theta) \rangle$ is the average value of the Legendre function for the state of interest. Similar to the global minima on PES, there are also two equivalent average structures. The average structure is calculated to be of $R = 3.7126 \text{ \AA}$, $\theta_1 = 13.7^\circ$, $\theta_2 = 95.2^\circ$, $\varphi = 173.6^\circ$ or $R = 3.7126 \text{ \AA}$, $\theta_1 = 166.3^\circ$, $\theta_2 = 95.2^\circ$, $\varphi = 6.4^\circ$, which corresponds to the third possible structure given in Ref. 24. Within the structure determined in this work, the terminal O nuclei of N₂O is closer to the N₂ monomer than the N end, indicating this structure is much more stable than the others. These calculated average parameters agree well with the experimental values, with a deviation of $\Delta R = 0.02 \text{ \AA}$, $\Delta \theta_1 = 0.4^\circ$, $\Delta \theta_2 = 3.4^\circ$. It is interesting to compare the structural parameters between local minima on the PES and the vibrational average values. For the intermolecular distance, the average R is 0.05 Å larger than that of the local minima. The deviation is 4.7° for θ_1 , but just 0.2° for θ_2 . The larger deviation occurring for N₂ monomer from its equilibrium value can be considered as an effect of large zero-point vibrational motion of the monomer in the complex.

C. Rotational levels and transition frequencies

The infrared spectra have been observed and analyzed in the ν_1 and ν_3 regions of N₂O monomer^{23,25,26} for ¹⁴N₂-¹⁴N₂O, and the pure rotational spectrum was studied by Leung²⁴ for

¹⁵N₂-¹⁴N₂O. These experimental studies provide us a large number of data to inspect the accuracy of the potential energy surface. For the microwave spectrum of ¹⁵N₂-¹⁴N₂O, 14 rotational transitions (7 *a*-type and 7 *b*-type) were assigned to the excited internal motion state and 4 rotational transitions (1 *a*-type and 3 *b*-type) were assigned to the ground internal motion state. This data is available as supplementary material for Ref. 24. Here, we give a detailed calculation for all the possible transitions with $J \leq 5$ and $K_a \leq 2$. A total of 67 transitions are obtained by using the molecular constants given in Ref. 24. For ¹⁴N₂-¹⁴N₂O, twenty-three ground state combination differences are obtained with $J \leq 5$ and $K_a \leq 2$ from the infrared spectra.^{23,25,26}

TABLE VII. The ground state combination differences obtained from infrared spectra^{23,25,26} with $J \leq 5$ and $K_a \leq 2$ and corresponding calculated values (in cm⁻¹).

J'	K_a'	K_c'	J''	K_a''	K_c''	Expt.	Cal.	Expt.-Cal.
1	1	0	2	0	2	0.107 76	0.109 05	-0.001 28
2	1	2	1	1	0	0.238 62	0.238 07	0.000 55
2	1	1	1	1	1	0.280 78	0.278 91	0.001 88
2	1	2	0	0	0	0.736 21	0.734 72	0.001 49
2	2	0	2	1	2	1.101 99	1.102 28	-0.000 28
2	2	0	2	0	2	1.448 49	1.449 4	-0.000 89
2	2	1	1	0	1	1.707 92	1.707 5	0.000 42
3	0	3	2	1	1	0.011 12	0.009 2	0.001 92
3	1	3	3	0	3	0.331 51	0.332 44	-0.000 94
3	2	2	2	2	0	0.389 51	0.387 25	0.002 26
3	2	1	2	2	1	0.390 64	0.388 54	0.002 11
3	1	2	2	1	2	0.436 44	0.433 52	0.002 93
4	0	4	3	1	2	0.123 65	0.121 18	0.002 48
4	1	4	3	1	2	0.436 21	0.434 84	0.001 38
4	2	3	3	2	1	0.518 11	0.515 35	0.002 77
4	2	2	3	2	2	0.522 33	0.519 63	0.002 71
4	0	4	2	0	2	0.906 02	0.901 82	0.004 23
5	0	5	4	1	3	0.228 28	0.226 23	0.002 05
5	1	5	5	0	5	0.290 94	0.291 39	-0.000 45
5	1	4	4	1	4	0.776 52	0.772 64	0.003 89
5	2	3	5	0	5	1.461 23	1.461 98	-0.000 74
5	2	4	4	0	4	2.098 84	2.096 45	0.002 4
5	2	3	3	0	3	2.623 79	2.618 78	0.005 03
RMSD							0.002 31	

TABLE VIII. Comparison of the spectroscopic parameters and the inertial defects $\text{N}_2\text{-N}_2\text{O}$ complex in the ground vibrational state.

Parameters	$^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$		$^{14}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$	
	Experiment ^a	Calculation	Experiment ^b	Calculation
A (MHz)	12 791.306 95 (16)	12 790.74	12 794.4 (15)	12 799.93
B (MHz)	2 014.982 44 (11)	2 004.16	2 100.73 (30)	2 090.85
C (MHz)	1 728.950 452 (72)	1 721.07	1 791.87 (27)	1 784.73
Δ_J (kHz)	10.526 2 (23)	8.87	6.4 (12)	9.60
Δ_{JK} (kHz)	393.368 (27)	376.48	348 (17)	409.82
δ_J (kHz)	-1.822 0 (30)	-1.60	-1.64 (18)	-1.95
δ_K (kHz)	-1.180 (55)	-0.75	-0.797 (74)	-0.953
Inertial defect	1.98	1.97	1.98	1.98

^aThese rotational constants given in Ref. 24.^bThese rotational constants given in Ref. 25.

The rotational energy levels for $J = 0\text{--}5$ of the ground vibrational state for the isotopomers $^{14}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ and $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ and their assignments are listed in Table V. The theoretical transition frequencies and their deviations from experimental values are listed in Tables VI and VII. We can see that the RMSD between the experimental and calculated values is better than 0.002 cm^{-1} and the maximum deviation is 0.0037 cm^{-1} with the transition $3_{22}\text{--}4_{13}$ for $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$. A nearly equivalent RMSD is obtained (0.0023 cm^{-1}) for the combination differences with the maximum deviation of 0.005 cm^{-1} for the dummy transition $5_{23}\text{--}3_{03}$. In order to compare the spectroscopic parameters with experimental values directly, the theoretical rotational energy levels (in keeping with the transitions calculated here, $J \leq 5$ and $K_a \leq 2$ levels are selected to fit, because the transitions with higher J and K_a are difficult to be observed in the microwave region) are used to fit with the same Hamiltonian used in the experiment. These levels were used to fit a Watson asymmetric rotor of the S -type reduction in the I' representation⁴² and the Hamiltonian can be expressed as follow:

$$\begin{aligned}
 H = & \frac{1}{2}(B+C)\hat{J}^2 + \left[A - \frac{1}{2}(B+C)\right]\hat{J}_a^2 \\
 & + \frac{1}{2}(B-C)(\hat{J}_a^2 - \hat{J}_c^2) - \Delta_J\hat{J}^4 \\
 & - \Delta_{JK}\hat{J}_a^2\hat{J}^2 - \Delta_K\hat{J}_a^4 - 2\delta_J\hat{J}^2(\hat{J}_a^2 - \hat{J}_b^2) \\
 & - \delta_K[\hat{J}_a^2(\hat{J}_b^2 - \hat{J}_c^2) + (\hat{J}_b^2 - \hat{J}_c^2)\hat{J}_a^2]. \quad (7)
 \end{aligned}$$

The fitting was performed by using the SPFIT program.⁴³ In keeping with experimental results, the value of quartic centrifugal distortion constant was fixed at the value of zero in the fitting. The obtained parameters show excellent agreement with the corresponding experimental values.^{23,24} As seen in Table VIII, the maximum deviation is only 10 MHz for the rotational parameter B . Within the nearly T-shape structure for $\text{N}_2\text{-N}_2\text{O}$, the monomer N_2 makes a small angle at the a -axis and N_2O is almost perpendicular to this axis. As mentioned above, N_2 monomer undergoes a large bending motion, which is possibly responsible for this deviation. The inertial defects of $^{14}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ and $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$ dimers are also listed in Table VIII. The calculated value is $1.97\text{ amu \AA}^2$ for $^{15}\text{N}_2\text{-}^{14}\text{N}_2\text{O}$, which is in excellent agreement with the experimental measurement of $1.98\text{ amu \AA}^2$.

The good agreement between the theory and experiment confirms the high accuracy of the *ab initio* PES. The transition frequencies and spectroscopic parameters predicted accurately may be attributed to two factors: First, taking the equilibrium structure and the average structure for comparison, both the vdW stretching between two monomers and the bending of N_2O monomer could be negligible in the zero-point motion; second, although there is larger bending ($\Delta\theta_1 = 4.7^\circ$) for N_2 molecule, this monomer exhibits a nearly perfect rigid rotor and makes a small angle at the a -axis, resulting in that the bending effect for N_2 monomer is also negligible. Therefore, the theoretical predictions reproduce the experimental results with an excellent agreement based on our four-dimensional PES at the rigid rotor approximation for N_2 and N_2O monomers.

IV. CONCLUSIONS

Theoretical studies of the potential energy surface and bound states are performed for the $\text{N}_2\text{-N}_2\text{O}$ vdW dimer. A four-dimensional intermolecular PES is constructed at the CCSD(T) level with aug-cc-pVTZ basis set supplemented with bond functions. Two equivalent local minima are found on this surface and correspond to two nearly T-shaped stable structures, in which the O atom in N_2O is closer to N_2 than N atom in N_2O . The dissociation energies of $\text{N}_2\text{-N}_2\text{O}$ are 334.714 cm^{-1} for the two equivalent local minima. Due to the space inversion of N_2 molecule in the dimer, each vibrational state of this complex splits into two subunits from the bound state calculations. The energy for each subunit (ground state) is -239.416 21 and $-239.415\text{ 96 cm}^{-1}$ with a zero-point energy of 95.298 cm^{-1} .

Three intermolecular fundamental vibrational states, namely, disrotation, torsion, and vdW stretch, are assigned from an analysis of their wavefunctions, but the conrotation vibrational mode could not be identified, due to the wavefunction mixed by another vibrational mode. A similar case exists in our previous work for T-shaped isomer for $\text{CO}_2\text{-N}_2\text{O}$. The calculated disrotation vibrational frequency (23.086 cm^{-1}) is in good agreement with the experimental measurement (22.334 cm^{-1}). The torsion vibrational mode is calculated to be 30.46 cm^{-1} , which could be helpful to carry out the further studies of combination bands. The quantum tunneling effects increase as the increment of vibrational frequency and

the splitting is more than 3.0 cm^{-1} between 25th and 26th roots in the even parity block.

Two equivalent average structures are determined to be $R = 3.7126\text{ Å}$, $\theta_1 = 13.7^\circ$, $\theta_2 = 95.2^\circ$, $\varphi = 173.6^\circ$ or $R = 3.7126\text{ Å}$, $\theta_1 = 166.3^\circ$, $\theta_2 = 95.2^\circ$, $\varphi = 6.4^\circ$, which correspond to the third possible structure given in Ref. 24. The calculated frequencies for the two isotopomers are inspected by 23 ground combination differences from infrared spectra for $^{14}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$ and 67 pure rotational transitions for $^{15}\text{N}_2\text{--}^{14}\text{N}_2\text{O}$. The deviation for all the transitions between the experimental and calculated values is less than 0.005 cm^{-1} and the RMSD is around 0.002 cm^{-1} . The good agreement between theory and experiment validates the high accuracy of this *ab initio* PES in the vicinity of van der Waals wells.

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