Improving Analysis of Infrared Spectra of van der Waals Complex with Theoretical Calculation: Applied to Xe–N₂O complex

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Abstract:

A section of infrared spectrum for Xe–N₂O has been recorded in the N₂O monomer ν_1 region, but just 5 rotational resolved lines can not make an effective rovibrational analysis. To improve the analysis of our observed spectrum for Xe–N₂O, a new method is developed based on the bound state calculations with three ab initio potential energy surfaces (PESs). The accuracy of this method is validated by the excellent agreement between theoretical and experimental results for 152 rovibrational transition frequencies with a root mean square deviation of 0.00075 cm⁻¹ and spectroscopic parameters with the deviation less than 0.6 MHz in the N₂O monomer ν_3 region. The rotational constants for the excited state are derived with the values of $A = 12716.1$, $B = 1075.2$, $C = 987.9$ MHz in the ν_1 region of N₂O monomer. The band origin of the spectrum is determined to be 1284.8760 cm⁻¹ with a red shift of 0.0273 cm⁻¹ compared with that of N₂O monomer in the ν_1 region. The excellent agreement between experimental and theoretical results confirms that this new method is extremely helpful to make a rovibrational analysis for the infrared spectrum of van der Waals complex.

Keywords: Van der Waals Complex; Infrared Spectrum; Xe–N₂O; Potential energy surface;

Bound state calculations

1. Introduction

Due to the great atmospheric interest of nitrous oxide [1], vdW complexes involving N₂O have drawn forth great interest and much research [2]. Rg–N₂O (Rg = He, Ne, Ar, Kr, Xe) complexes are considered as the typical system to investigate intermolecular interaction and have been extensively investigated both experimentally [3-15] and theoretically [16-27]. Ar–N₂O is the first complex of this system, which has been widely experimentally studied using the microwave [3-5] and infrared [6-8] spectroscopic techniques. These spectroscopic results showed that the structure of Ar–N₂O complex is nearly T-shaped with the oxygen end of the N₂O monomer slightly tilted towards the Ar atom.

Now, the Rg–N₂O (Rg = Ne, Ar, Kr and Xe) complexes have been well studied in the ν_3 region of N₂O monomer. The intermolecular distance (R) varies from 3.24 to 3.78 Å and the angle (θ) between the intermolecular axis and the N–N–O axis varies from 82.0 to 84.6°. The vibrational shifts for Rg–N₂O (Rg = Ne, Ar, Kr and Xe) were well explained based on the Buckingham intermolecular potential and this model can be also applied to the similar complexes of Rg–CO₂/OCS successfully [9]. Recently, the validity of this model was further confirmed by the results for Rg–N₂O (Rg = Ne, Ar, Kr) in the ν_1 region of N₂O monomer [15].

In theory, the dynamics of Rg–N₂O (Rg = Ne, Ar, Kr and Xe) have also been well established based on the high resolution intermolecular potential and bound state calculations [16-22]. The ab initio PESs give the intermolecular distance of 3.16, 3.47, 3.54 and 3.80 Å for Ne–N₂O [16], Ar–N₂O [17], Kr–N₂O [18] and Xe–N₂O [19], which are very close to their corresponding values of the effective distances determined by experiment. Since the infrared spectra of He–N₂O were investigated by Tang and McKellar [11], there have been several theoretical reports on this complex [23-27]. Good agreement has been achieved between the calculated spectra and the experimental results. The three-dimensional and four-dimensional ab initio PESs not only can be used to predict vibrational shifts accurately for ⁴He–N₂O and ³He–N₂O, but also can be applied to study the dynamics of He_N–N₂O cluster using the path integral Monte Carlo simulation [26, 27].

In this paper, we select Xe–N₂O complex as the object of theoretical and experiment studies. It attributes several factors: Firstly, the first PES was made for Xe–N₂O complex by Chen et al. [19] and the rovibrational transitions were predicted with the RMSD of 0.073 cm^{−1}. Therefore, this potential for Xe–N₂O is not accurate enough. Recently, a three-dimensional potential has been reported by Wang et al. [22]. Based on this potential, the calculated precision has been greatly improved, but the RMSD of 152 rovibrational transitions is also more than 0.016 cm^{−1}, which is still not accurate enough to help the spectral assignment. Besides, the infrared spectrum is just observed and analyzed in the ν_3 region of N₂O, and we can not get knowledge of different dynamical information of Xe–N₂O complex upon ν_1 vibrational excitation of N₂O monomer. In fact, a section of spectrum was observed seven years ago, but just 5 rotational resolved lines are not enough to perform an effective rovibrational analysis even if the ground rotational constants were given. Here, we construct three two-dimensional PESs for the ground and excited states of

Xe–N₂O complex. Based on the results of bound state calculations and the reported rotational constants [9], we make a rovibrational analysis of our observed spectrum for Xe–N₂O using a new method. The excellent agreement between experimental and theoretical results confirms that this new method is extremely helpful to make a rovibrational analysis for the infrared spectrum of van der Waals complex.

2. Computational and experimental details

2.1. Theoretical calculations

The potentials for Xe–N₂O are constructed at the rigid rotor approximation and the N–N and N–O bond lengths used here are listed in Table 1 for its ground and excited states of N₂O monomer [28, 29]. We obtain the bond lengths for excited states of N₂O monomer by using the basic theory of a linear triatomic molecule [30]. The detailed calculation is presented in Supplementary data.

The intermolecular energy of each geometry was calculated using the supermolecular method at the level of single and double excitation coupled-cluster method with a noniterative perturbation treatment of triple excitations [CCSD(T)] [31]. The augmented correlation consistent polarized valence triple-zeta (aug-cc-pVTZ) basis sets of Woon and Dunning [32] are employed for N and O atoms, while the augmented correlation-consistent polarized valence quintuple-zeta (aug-cc-pV5Z-PP) basis set was chosen for Xe atom [33, 34]. The bond functions (3s3p2d1f1g) (for 3s and 3p, $\alpha = 0.9, 0.3, 0.1$; for 2d, $\alpha = 0.6, 0.2$; for 1f and 1g, $\alpha = 0.3$) [35] are also used at the middle point of the intermolecular distance R . The full counterpoise procedure of Boys and Bernardi [36] is employed to correct the basis set superposition error (BSSE). All the calculations are carried out using the Molpro 2010 software package [37]. The ab initio potential energy grids were selected for Xe–N₂O with 31 the radial grids from 1.50 to 10.00 Å and 13 angular grids from 0° to 180° in the step of 15°. The three two-dimensional PESs are constructed by executing two one-dimensional interpolations with the Lagrange polynomial formula, this interpolation scheme has employed in the previous study [38].

Within the rigid rotor approximation for the linear N₂O molecular, the Hamiltonian of the Xe–N₂O complex in Jacobi coordinates can be written as [39]:

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{2\mu R^2} (\hat{J} - \hat{j})^2 + B_{N_2O} \hat{j}^2 + V(R, \theta) \quad (1)$$

where μ is the reduced mass of the Xe–N₂O complex, $\hat{J}$ is total angular momentum and $\hat{j}$ is the angular momentum for N₂O monomer, and B_{N_2O} is the rotational constant of N₂O with the values of 0.419011, 0.417255, and 0.415560 cm^{−1} in its ground and excited vibrational states of N₂O monomer [28, 29]. The wave function used here was given in Ref. 38. The bound state calculation program is OpenMP parallelized and the PARPACK software package [40] is applied to solve the eigenvalues and eigenfunctions of the bound states. The rovibrational bound states were calculated with the total angular momentum up to $J_{\text{tot}} = 6$ for the ground and excited states. In our calculations we used 200 sine-DVR points for the R coordinate, 246 basis functions of associated Legendre polynomials, and 200 DVR grid points for θ . The convergence accuracy of eigenvalues is evaluated to be better than 0.001 cm^{−1}.

2.2. Experiment

The spectrometer used to record the spectrum of Xe–N₂O complex has been in detailed described in Ref. 13. The Xe–N₂O complex was formed by expanding a mixture of 0.5% N₂O and 15% Xe in the He carrier gas through two 800-mm pin-hole nozzles at room temperature. Backing pressure was 3 atm for Xe–N₂O. The spectrum was calibrated against the accurate line positions of N₂O using a confocal etalon with a free spectral range of 0.01 cm^{−1}. Our experimental accuracy of the measurement was estimated to be better than 0.0005 cm^{−1} and the spectrum is analyzed and fit using the SPFIT program [41].

3. Results and analysis

3.1. Ab initio PESs and bound state calculations

The contour plots of $V(R, \theta)$ are shown in Figure 1. The three intermolecular PESs have very similar features and each potential is characterized by a global T-shaped minimum, a linear local minima, and two saddle points located at the sides of global minimum. For the ground state, the global minimum is located at $R = 3.75$ Å and $\theta = 87.0^\circ$ with a depth of 283.933 cm^{−1}. The local minimum corresponds to the linear geometry at $R = 4.83$ Å, $\theta = 0.0^\circ$ with a depth well of 162.017

cm^{-1} . The saddle point 1 connecting the global and the local minimum is located at $R = 4.69 \text{ \AA}$, $\theta = 30.0^\circ$ with a height of only 3.518 cm^{-1} , relative to the linear local minimum. The saddle point 2 connects the two global minima is located at $R = 5.16 \text{ \AA}$, $\theta = 180.0^\circ$ with a height of 153.482 cm^{-1} , relative to the nearly T-shape minimum. The geometries and energies of the minima and saddle points on the ab initio PESs are listed in Table 2 including the previous results for comparison. The previous PES for Xe-N₂O was performed by Chen et al. at the CCSD(T) level in 2004 [19]. As seen in Table 2, the global minimum was located at $R = 3.80 \text{ \AA}$ and $\theta = 88.0^\circ$ with a depth of 256.510 cm^{-1} on this potential. To our knowledge, the geometry of global minimum presented in Ref. 9 is $R_m = 3.7806 \text{ \AA}$, $\theta = 82.99^\circ$ and $V_m = -213.21 \text{ cm}^{-1}$, indicated that both results are in good agreement with that of previous determination. For the excited states, the well depth of the global minimum and the local minimum on the potentials for both excited states are deeper than those of ground state, indicated that there is a slight strengthen of the vdW interaction upon vibrational excitation and a red shift is to occur for the infrared spectra of Xe-N₂O in the ν_1 and ν_3 region of N₂O monomer.

The bound energy of vibrational ground state for the T-shaped structure of Xe-N₂O complex is calculated to be -246.712 cm^{-1} , corresponding to a zero-point energy of 36.221 cm^{-1} . For the linear structure of Xe-N₂O, the bound energy of vibrational ground state is calculated to be -141.863 cm^{-1} , corresponding to a zero-point energy of 20.154 cm^{-1} . The ground energy level is more than 15 cm^{-1} higher than that of the saddle point 1, indicated that the obvious quantum delocalization effect will occur. For the two excited states, the bound energy, as well as the zero-point energy is almost equivalent to those of ground state. The bound energy of vibrational excited states for the T-shaped structure of Xe-N₂O complex is calculated to be -246.845 and -246.972 cm^{-1} for the monomer ν_1 and ν_3 excited states, respectively.

The intermolecular vibrational states can be characterized by two quantum numbers (n_s , n_b), where n_s stands for the van der Waals stretching mode and n_b is the bending mode. Here, just the intermolecular modes of ground state are calculated and discussed in this paper. The frequencies for the first twelve vibrational modes are listed in Table 3, including their vibrational assignments. These vibrational states are assigned unambiguously via the wavefunction analysis. Figure 2 is R - θ contour plots of the wavefunctions for the assigned vibrational states of Xe-N₂O complex.

The ground state (0, 0) is localized in the T-shaped global minimum, and the second and third roots are attributed to the intermolecular stretching (1, 0) and bending (0, 1) modes with the vibrational frequencies of 33.155 and 34.021 cm^{-1} , respectively. These results are in agreement with those presented in Chen's work. The following three vibrational modes can be assigned at the sequence of (2, 0), (0, 2), (1, 1) with the vibrational frequencies of 61.627, 62.081 and 66.770 cm^{-1} , respectively. This sequence of vibrational modes is not consistent with those given in Ref. 19. The reason for this difference can be attributed to the factor that the vibrational frequency for the two fundamental modes is almost equivalent in our work, but the energy difference was calculated to be 3.5 cm^{-1} given in Ref. 19. Due to lack of experimental results, it is difficult to confirm which result is more reliable.

We also make an assignment for the linear isomer and the R - θ contour plots of the wavefunctions were presented in Figure 3. As seen in Figure 3, there is obvious delocalization effect for the ground wavefunction because the zero-point energy of the linear structure is larger than the barrier height. The following three excited vibrational modes of the linear structure are all assigned as the intermolecular stretching modes with the vibrational frequencies of 25.226, 49.561 and 66.506 cm^{-1} , respectively.

3.2. Infrared spectra

The frequencies of rotational energy levels and their assignments are listed in Table S1 in the supplementary data. A section of spectrum with five lines recorded in the ν_1 region of N_2O monomer for $\text{Xe-N}_2\text{O}$ was presented in Figure 4. The rotational constants of the ground state have been determined to be $A = 12769.5(5)$, $B = 1075.5(2)$, $C = 986.9(1)$ MHz by Herrebout et al. [9]. Based on these rotational constants and bound states results, we make a rovibrational analysis of our observed spectrum. Using the data listed in Table S1, an energy difference can be obtained using the following expression

$$\Delta E = E_{J', K_a' K_c'} - E_{J'', K_a'' K_c''} \quad (2)$$

where all the quantum numbers (J , K_a , and K_c) take the same values for the ground and excited states, namely $J' = J''$, $K_a' = K_a''$ and $K_c' = K_c''$. A diagram is presented in Figure 5 for energy differences of the rotational energy levels with $J \leq 5$ and $K_a \leq 4$. As seen in Figure 5, the

calculated deviation of energy differences can be significant reduced by above-mentioned method, so it is more reliable to make a rovibarbional analysis of our observed spectrum using these energy differences with the rotational constants of ground states fixed at the values determined by Herrebout et al. [9] for Xe–N₂O complex. The derived rotational constants are listed in Table 4 for the excited states upon the ν_1 and ν_3 excitation of N₂O monomer. Based on these rotational constants, the five lines presented in Figure 4 can be assigned as the $R(3)$ — $R(7)$ of R -branch unambiguously. The line frequencies and their assignments are listed in Table 5, including the corresponding spectral lines of the monomer ν_3 excited state. Using the line frequencies and derived rotational constants, the band origin of our observed spectrum is determined to be 1284.8760 cm⁻¹ with a red shift of 0.0273 cm⁻¹ compared to that of N₂O monomer. Similarly, the band origin is determined to be 2223.26592 cm⁻¹ in the N₂O monomer ν_3 band, which is in excellent agreement with the experimental result with a deviation of only 0.0001 cm⁻¹. To illustrate the accuracy of our calculated method, we give a detailed calculation for the observed transitions in the ν_3 region of N₂O monomer. These results were listed in Table S2 and the RMSD of 152 rotational transitions is 0.00075 cm⁻¹, which is very close to the value (0.00049 cm⁻¹) of experimental fit. The simulated spectra of Xe–N₂O are also shown in Figure 4. The rotational temperature and Gaussian line-width of simulated spectra are set at 1.5 K and 0.004 cm⁻¹, respectively. The simulated spectrum of Xe–N₂O reproduces the observed spectrum very well (see the small section shown in the box of Figure 4).

4. Discussion and conclusions

4.1. Structural parameters

The average structural parameters $\langle R \rangle$ and $\langle \theta \rangle$ for a vibrational state can be determined from the related wavefunctions using the following formulas [42]

$$\left\langle \frac{1}{R^2} \right\rangle \approx \frac{1}{\langle R^2 \rangle} \quad \text{and} \quad P_2(\cos \langle \theta \rangle) = \langle P_2(\cos \theta) \rangle \quad (3)$$

where 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. The calculated structural parameters of the ground and excited states for Xe–N₂O complex are listed in Table 6. As seen in the Table 6, the average

structural parameter for the intermolecular distance R of Xe–N₂O complex is calculated to be 3.809 Å in the case of T-shaped isomer, which is in good agreement with the experimental determination with a difference of 0.021 Å. The corresponding rotational angle θ was determined to be 82.94°, which just has a deviation of 0.05°. For the excited states, both the calculated values and variable trend for these parameters are also in good agreement with the experimental results. In the case of linear isomer, the intermolecular distance is calculated to be 4.62 Å and the corresponding angle is 32.89°. However, there is obvious delocalization effect existing at the radial and angular directions for the linear isomer, we think that these parameters can not be calculated accurately.

It is very interesting to compare the structural parameters between local minima on the PES and the vibrationally average values. For the intermolecular distance, the deviation between the average value and the equilibrium structure is quite small, which is about 0.05 Å for the three vibrational states. For the rotational angles, there are great deviations between the average and equilibrium structure, and the values are about 4.0° for the three vibrational states. The larger deviations of $\langle\theta\rangle$ from their equilibrium values can be thought of as an effect of librational motion of N₂O monomer in the complex.

4.2. Vibrational shifts

As seen in Table S1, there are red shifts of 0.133 and 0.260 cm⁻¹ upon the ν_1 and ν_3 vibrational excitation of N₂O, respectively. Compared with the experimental value of 0.0273 and 0.491 cm⁻¹ in the ν_1 and ν_3 region of N₂O, our predicted vibrational shifts are in qualitative agreement with the experimental observation. To our knowledge, the band origin shifts for Rg–N₂O (Rg = Ne, Ar, Kr, and Xe) have been well explained using a simple model based on the Buckingham potential by Herrebout et al. [9]. Our previous work has proved that this model is also suitable to the Rg–N₂O complexes (Rg = Ne, Ar, and Kr) in the ν_1 region of N₂O monomer. Here we will examine whether this model can be applicable to Xe–N₂O in this spectral region. These results are presented in Figure 6. As seen in Figure 6, the plot of $\Delta\nu/(C_6/R_m^6)$ versus $3\beta/R_m$ for Rg–N₂O (Rg = Ne, Ar, Kr and Xe) also makes a linear relationship in the ν_1 region of N₂O monomer. The intercept is $\Delta C_6/C_6 = 0.00487$ and the slope is $\langle\Delta q^2\rangle = 0.00167$, while the corresponding values in the ν_3 region of N₂O [9] are 0.00119 and 0.0037, respectively. In our

previous work [15], the band origin shift of Xe–N₂O in the ν_1 region of N₂O was predicted to be -0.0333 cm^{-1} by extrapolation from the plot for Rg–N₂O (Rg = Ne, Ar and Kr). This result reproduces our observed result with good accuracy, indicated that the simple mode based on the Buckingham potential can give a precise prediction of vibrational shifts for Rg–N₂O complexes (Rg = Ne, Ar, Kr and Xe).

In conclusion, a new theoretical and experimental study of the potential energy surface, bound states, and infrared spectrum are performed for Xe–N₂O complex. Three two-dimensional PESs are constructed for Xe–N₂O complex at the CCSD(T) level supplemented with bond functions. Intermolecular vibrational states for both T-shaped and linear isomers are assigned from the analysis of their wavefunctions. The wavefunction of linear isomer undergoes obvious quantum delocalization effect, indicated the spectrum of linear isomer can not be observed in experiment. The band origins for both excited states are predicted to be red shift with the values of 0.133 and 0.260 cm^{-1} in the monomer ν_1 and ν_3 region, respectively. Compared with the experimental values, our predicted vibrational shifts are in at least qualitative agreement with the experimental observations.

A section of infrared spectrum (including 5 rotational resolved lines) for Xe–N₂O has been recorded in the N₂O monomer ν_1 region using an infrared tunable diode laser spectrometer in conjunction with a free supersonic jet expansion. A new method is developed to make a rovibrational analysis of our observed spectrum for Xe–N₂O. The rotational constants for the excited state are derived with the values of $A = 12716.1$, $B = 1075.2$, $C = 987.9$ MHz and the band origin of the spectrum is determined to be 1284.8760 cm^{-1} with a red shift of 0.0273 cm^{-1} compared to that of N₂O monomer in the ν_1 region. The excellent agreement between experimental and theoretical results confirms that this new method is extremely helpful to make a rovibrational analysis for the infrared spectrum of van der Waals complex.

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Reference:

- [1] See http://en.wikipedia.org/wiki/Nitrous_oxide for the introduction of Nitrous oxide.
- [2] S. E. Novick, Bibliography of rotational spectra of weakly bound complexes; Electronic updates are available on the web at https://wesfiles.wesleyan.edu/home/snovick/SN_webpage/vdw.pdf, 2015.
- [3] C. H. Joyner, T. A. Dixon, F. A. Baiocchi, W. Klemperer, J. Chem. Phys. 75 (1981) 5285-5290.
- [4] H. O. Leung, D. Gangwani, J.-U. Grabow, J. Mol. Spectrosc. 184 (1997) 106-112.
- [5] M. S. Ngari, W. Jäger, J. Mol. Spectrosc. 192 (1998) 452-454.
- [6] H. Hodge, G. D. Hayman, T. R. Dyke, B. J. Howard, J. Chem. Soc. Faraday Trans. 82 (1986) 1137-1142.
- [7] T. A. Hu, E. L. Chappell, S. W. Sharpe, J. Chem. Phys. 98 (1993) 6162-6169.
- [8] G. Gimmler, M. Havenith, J. Mol. Struct. 599 (2001) 117-123.
- [9] W. A. Herrebout, H.-B. Qian, H. Yamaguchi, B. J. Howard, J. Mol. Spectrosc. 189 (1998) 235-243.
- [10] M. S. Ngari, W. Jäger, J. Mol. Spectrosc. 192 (1998) 320-330.
- [11] J. Tang, A. R. W. McKellar, J. Chem. Phys. 117 (2002) 2586-2591.
- [12] X. G. Song, Y. J. Xu, P.-N. Roy, W. Jäger, J. Chem. Phys. 121 (2004) 12308-12314.
- [13] D. S. Zhu, R. B. Wang, R. Zheng, G. M. Huang, C. X. Duan, J. Mol. Spectrosc. 253 (2009) 88-91.
- [14] R. Zheng, D. S. Zhu, Y. Zhu, C. X. Duan, J. Mol. Spectrosc. 263 (2010) 174-177.
- [15] R. Zheng, Y. Zhu, S. Li, C. X. Duan, Mol. Phys. 109 (2011) 823-830.
- [16] H. Zhu, D. Q. Xie, G. S. Yan, Chem. Phys. Lett. 351 (2002) 149-157.
- [17] H. Zhu, D. Q. Xie, G. S. Yan, J. Comput. Chem. 24 (2003) 1839-1845.
- [18] R. Chen and H. Zhu, J. Theo. Comput. Chem. 7 (2008) 1093-1102.
- [19] J. X. Chen, H. Zhu, D. Q. Xie and G. S. Yan, Acta Chimica Sinica 62 (2004) 5-9.
- [20] J. H. Wang, Y. L. Han, Z. Li, E. Y. Feng, W. Y. Huang, Mol. Phys. 111 (2013) 771-777.
- [21] Z. Wang, E. Feng, C. Zhang, C. Sun, Chem. Phys. Lett. 626 (2015) 43-48.
- [22] Z. Wang, E. Feng, C. Zhang, C. Sun, Chem. Phys. Lett. 638 (2015) 66-71.
- [23] B.T. Chang, O. Akin-Ojo, R. Bukowski, K. Szalewicz, J. Chem. Phys. 119 (2003) 11654-11670.
- [24] Y. Z. Zhou, D. Q. Xie, J. Chem. Phys. 120 (2004) 8575-8581.
- [25] Y. Z. Zhou, D. Q. Xie, D. H. Zhang, J. Chem. Phys. 124 (2006) 143317.
- [26] L. C. Wang, D. Q. Xie, H. Guo, H. Li, R. J. Le Roy, P. N. Roy, J. Mol. Spectrosc. 267 (2011) 136-143.
- [27] L. C. Wang, D. Q. Xie, R. J. Le Roy, P. N. Roy, J. Chem. Phys. 137 (2012) 104311.
- [28] J.-L. Teffo, A. Chedin, J. Mol. Spectrosc. 135 (1989) 389-409.
- [29] A. G. Maki, and J. S. Wells, *Wavenumber calibration tables from heterodyne frequency measurements*, NIST Special Publication 821, 1991.
- [30] G. H. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand

Reinhold, New York, 1945.

- [31] C. Hampel, K. Peterson, and H. J. Werner, Chem. Phys. Lett. 190 (1992) 1-12.
- [32] D. E. Woon and T. H. Dunning, J. Chem. Phys. 98 (1993) 1358-1371.
- [33] K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, J. Chem. Phys. 119 (2003) 11113.
- [34] Q. Wen and W. Jäger, J. Chem. Phys. 122 (2005) 214310.
- [35] T. B. Pedersen, B. Fernandez, H. Koch, and J. Makarewicz, J. Chem. Phys. 115 (2001) 8431.
- [36] S. F. Boys and F. Bernardi, Mol. Phys. 19 (1970) 553-566.
- [37] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz et al., MOLPRO, version 2010.1, a package of ab initio programs, 2010, see <http://www.molpro.net>.
- [38] L. M. Zang, W. Dai, L. M. Zheng, C. X. Duan, Y. P. Lu, and M. H. Yang, J. Chem. Phys. 140 (2014) 114310.
- [39] S. Y. Lin and H. Guo, J. Chem. Phys. 117 (2002) 5183-5191.
- [40] R. Lehoucq, D. C. Sorensen, and C. Yang, ARPACK User's Guide: Solution of Large-Scale Eigenvalue Problems with Implicitly Restarted Arnoldi Methods, SIAM, Philadelphia, PA, 1998 (<http://www.caam.rice.edu/software/ARPACK>).
- [41] H. M. Pickett, J. Mol. Spectrosc. 148 (1991) 371-377.
- [42] L. A. Lajohm, P. A. Christiansen, R. B. Ross, T. Atashroo, W. C. Ermler, J. Chem. Phys. 87 (1987) 2812-2824.
- [43] J. Zhu, Y.-P. Lu, X.-R. Chen, and Y. Cheng, Eur. Phys. J. D, 33 (2005) 43-48.

Figure Captions:

Figure 1 Contour plots of the intermolecular potential energy surface for the ground and excited states of Xe–N₂O complex, R in angstrom and θ in degree. (a) the PES of ground state, (b) the PES of excited state for monomer ν_1 mode, (c) the PES of excited state for monomer ν_3 mode.

Figure 2 The R - θ contour plots of the wavefunctions for the T-shaped isomer for ground state.

Figure 3 The R - θ contour plots of the wavefunctions for the linear isomer for ground state.

Figure 4 Observed (upper) and simulated (lower) spectra of Xe–N₂O complex in the ν_1 region of N₂O. The rotational temperature of 1.5K and a Gaussian line-width of 0.004 cm⁻¹. The line labeled with asterisk belongs to the N₂O monomer.

Figure 5 The energy differences for the ground and excited states between experiment and theoretical calculation based on PES I and PES III, G.L. stands for the energy of ground state and E.L. is the energy level of ν_3 monomer excited state in the figure.

Figure 6 Relationship between $[\Delta\nu/(C_6/R_m^6)]$ and $(3\beta/R_m)$ for the complexes Rg–N₂O (Rg = Ne, Ar, Kr, and Xe) from a model based on the Buckingham intermolecular potential.

Table 1 The bond lengths (in Å) of N₂O used to construct the potentials.

Parameters	Ground state	Monomer ν_1 excited state	Monomer ν_3 excited state
r_e (N–O)	1.1273	1.1297	1.1319
r_e (N–N)	1.1851	1.1876	1.1900

Table 2 The important geometries and corresponding energy on the potential energy surfaces (R in angstrom, angles in degree and energy in cm⁻¹).

Vibrational state	Ground state	Monomer ν_1 state	Monomer ν_3 state	Ref. 19
Global minimum	(3.75, 87.0, -283.933)	(3.75, 87.0, -284.008)	(3.75, 87.0, -284.078)	(3.80, 88.0, -256.510)
Local minimum	(4.83, 0.0, -162.017)	(4.83, 0.0, -162.538)	(4.83, 0.0, -163.046)	(4.95, 0.0, -107.570)
Saddle point 1	(4.69, 30.0, -158.499)	(4.68, 31.0, -158.899)	(4.68, 31.0, -159.288)	(4.84, 27.6, -102.750)
Saddle point 2	(5.16, 180.0, -130.451)	(5.17, 180.0, -130.582)	(5.17, 180.0, -130.718)	—

Table 3 The intermolecular vibrational energy levels (in cm⁻¹) and their assignments (n_s , n_b) for Xe–N₂O complex.

This work			Ref. 19		
Assignment	Energy	Frequency	Assignment	Energy	Frequency
Nearly T-shape isomer					
(0, 0)	-246.712	0.00	(0, 0)	-219.94	0.00
(1, 0)	-213.598	33.115	(1, 0)	-188.78	31.16
(0, 1)	-212.691	34.021	(0, 1)	-184.31	35.63
(2, 0)	-185.085	61.627	(2, 0)	-160.96	58.98
(0, 2)	-184.632	62.081	(1, 1)	-156.72	63.22
(1, 1)	-179.942	66.770	(0, 2)	-151.10	68.84
(3, 0)	-162.220	84.492	(3, 0)	-136.93	83.01
(0, 3)	-161.552	85.160	(2, 1)	-131.69	88.25
(2, 1)	-153.058	93.655	(1, 2)	-127.44	92.50
(1, 2)	-151.293	95.419	(0, 3)	-120.85	99.09
(0, 4)	-145.675	101.038	(0, 4)	-116.77	103.17
(4, 0)	-144.588	102.124	(4, 0)	-109.81	110.13
Linear isomer					
(0, 0)	-141.863	0.00			
(1, 0)	-116.637	25.226			
(2, 0)	-92.302	49.561			
(3, 0)	-75.357	66.506			

Table 4 The determined spectroscopy parameters for Xe–N₂O complex.

Parameters	Experiment ^a		This work	
	Ground state	Monomer ν_3 state	Monomer ν_1 state	Monomer ν_3 state
A /MHz	12769.5(5)	12663.8(3)	12716.1	12664.5
B /MHz	1075.5(2)	1075.0(2)	1075.22	1074.96
C /MHz	988.4(1)	986.9(1)	987.85	987.31
ν / cm ⁻¹	—	2223.22603(9)	1284.87591 ^b	2223.26592 ^c

^a These values given in Ref. 9.

^b The band origin of ν_1 excited state is derived from our observed spectral lines.

^c This value is derived from the transition frequencies of 4₁₄—3₀₃, 5₁₅—4₀₄, and 6₁₆—5₀₅ given in Ref. 9.

Table 5 Observed and Calculated transition frequencies (in cm^{-1}) for Xe–N₂O in the N₂O monomer ν_1 and ν_3 region

Excited state			Ground state			N ₂ O monomer ν_1 region		N ₂ O monomer ν_3 region	
J	K_a	K_c	J	K_a	K_c	Frequencies	$\Delta\nu$ (Obs.-Calc.)	Frequencies ^a	$\Delta\nu$ (Obs.-Calc.)
4	1	4	3	0	3	1285.52664	0.00029	2223.91455	0.00035
5	1	5	4	0	4	1285.58774	-0.00014	2223.97548	-0.00002
6	1	6	5	0	5	1285.64781	-0.00017	2224.03523	-0.00016
7	1	7	6	0	6	1285.70714	0.00035	2224.09373	-0.00018
8	1	8	7	0	7	1285.76412	-0.00023	2224.15090	-0.00024

^a These values given in Ref. 9.

Table 6 The structural parameters for Xe–N₂O complex.

Vibrational state	Experiment ^a		This work	
	R (Å)	θ (degree)	R (Å)	θ (degree)
Ground state	3.7806	82.99	3.8090	82.94
Monomer ν_1 region	—	—	3.8095	82.94
Monomer ν_3 region	3.7824	83.00	3.8100	82.94

^a These values given in Ref. 9.

(a) PES I

(b) PES II

(c) PES III