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Three-dimensional Potential Energy Surface and Bound States of the Ar₂-Ne Complex

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The first three-dimensional interaction potential energy surface (PES) of the Ar₂-Ne complex is developed using the single and double excitation coupled cluster theory with noniterative treatment of triple excitations CCSD(T). The aug-cc-pVQZ basis sets are employed for all atoms, including an additional (3s3p2d2f1g) set of midpoint bond functions. The calculated single point energies are fitted to an analytic two-dimensional potential model at each of seven fixed r_{Ar_2} values. The seven model potentials are then used to construct the three-dimensional PES by interpolating along $(r-r_e)$ using a sixth-order polynomial. The PES is used in the following rovibrational energy levels calculations. The comparisons of theoretical transition frequencies and spectroscopic constants with the experimental results are given.

Key words: Ar₂-Ne complex, Potential energy surface, Rotational spectra

I. INTRODUCTION

Weakly bound van der Waals dimers and trimers are very important to understand the weak intermolecular forces and molecular dynamics. Among the smallest and simplest systems capable of molecular rearrangements, they exhibit wide amplitude bending and stretching motions. The high-resolution spectra of them are likely to provide detailed information on the non-additivity of intermolecular forces. During the past decades, these complexes have been the focus of intense experimental and theoretical studies [1–10]. Rg₂X (X is also a rare gas atom) is a kind of typical system of them, the complexes of which are often highly asymmetric rotor systems with irregular spectroscopic patterns. Large amplitude intermolecular motions of these weakly bound systems make the spectroscopic search and assignment procedures extremely challenging.

In the experiment, Xu *et al.* measured the pure rotational spectra of different isotopomers of the rare gas trimer Ne₂Kr and Ne₂Xe in their ground vibrational states using a Balle-Flygare type cavity pulse microwave Fourier transform spectrometer [6]. Rotational constants were evaluated, from which the geometries of the complexes were derived. In 1997, the spectra of ternary noble gas clusters Ar₂Ne and Ne₂Ar including various isotopomers with a Fourier transform were measured by Xu *et al.* [8]. Accurate rotational and centrifugal distortion constants were obtained, and the rotational constants were used to derive effective structural pa-

rameters for these systems.

During the theoretical investigations, Ernesti *et al.* constructed pairwise additive potential energy surfaces (PES) for different Rg₂X systems including Ne₂Kr, Ne₂Xe, and Ne₂Ar, then used the potentials to calculate the properties of the systems, and obtained the results that were substantially different from the experimental values [7]. They attributed the discrepancies to the uncertainties in the pair potentials. Then, Han *et al.* performed hyperspherical calculations on the $J=0$ bound states for Ne₂Ar and Ar₂Ne, and the rotational constants were obtained by vibrational averaged calculation [10]. The pairwise-additive potential was also used in the calculation. However, these works all neglected the Coriolis coupling and only considered the vibration of trimers, and therefore couldn't give an explicit explanation for experimental rotational spectra.

In this work, we study the *ab initio* determination of a three-dimensional PES for the Ar₂-Ne trimer for the first time. The PES is used in the following rovibrational energy levels calculations. The comparisons of predicted transition frequencies and spectroscopic constants with the experimental results are given.

II. COMPUTATION METHOD

A. Calculations of three-dimensional potential

In theoretical works on van der Waals complexes (Rg-diatom complexes for example), one customarily uses the vibrationally adiabatic (averaged) potential [11–13]. When the vibrational motion of the monomeric molecule is much faster than that of intermolecular motions in the complex, this approximation can provide a good explanation for the experimental re-

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sults. However, in the cases of Rg-dimer, like in the title van der Waals complex, the energies of intermolecular motions are comparable to that of vibrational motion of the monomer. The vibrationally adiabatic potential is thus inadequate. The full-dimensional interaction potential energy surface of the complex is required.

In this work, the PES for the Ar₂-Ne complex is calculated by the single and double excitation coupled cluster theory with noniterative treatment of triple excitations CCSD(T) method. The Dunning's aug-cc-pVQZ basis sets [14] are used for the Ne and Ar atoms with an additional set of (3s3p2d2f1g) midpoint bond functions [3]. The supermolecule approach is employed to get the intermolecular potential energy for each configuration. The full counterpoise procedure of Boys-Bernardi [15] is used to correct for the basis set superposition error. Calculations are performed. Jacobi coordinates are used including 7 values of the Ar₂ bond length r : 5.9, 6.3, 6.7, 7.127, 8.0, 9.2, 10.9 a₀, 23 values of the intermolecular separation, *i.e.* the distance between the Ne atom and the center of mass of Ar₂ molecule R : 4.0, 4.5, 5.0, 5.2, 5.5, 5.8, 6.0, 6.2, 6.8, 7.0, 7.2, 7.5, 8.0, 8.5, 9.0, 9.5, 10, 11, 12, 13, 15, 17, 19 a₀, and 8 angles between R and r θ from 0° to 90°: 0°, 10°, 20°, 40°, 60°, 80°, 85°, 90°, resulting in a PES consisting of a total of 1288 configurations. The calculations are performed with MOLPRO 2006 package [16].

The complete three-dimensional PES $V(R, r, \theta)$ of Ar₂-Ne is constructed by two steps. First, we construct seven two-dimensional PESs at each values of $r=5.9, 6.3, 6.7, 7.127, 8.0, 9.2,$ and 10.9 a₀ using the potential model proposed by Bukowski *et al.* [17]. Here, 7.127 a₀ is the equilibrium distance r_e of the Ar₂ dimer. In order to obtain the most reliable fit, in particular for the long-range part of the potential, we follow a two-step nonlinear least squares fit procedure [18, 19]. Those configurations with energies more than 500 cm⁻¹ are excluded from the fit. Figure 1 plots contours of the potential surfaces at $r=7.127$ a₀. Second, the seven two-dimensional PESs are used in the following construction of the three-dimensional PES by interpolating along $(r-r_e)$ using a sixth-order polynomial. The root-mean-square error is 0.061483 cm⁻¹, and the maximum absolute deviation is 0.4078 cm⁻¹. The three-dimensional PES constructed in this procedure is highly reliable as shown in our previous works [12, 13, 18, 19]. The PES can be obtained on request.

B. Bound state calculation

The bending and stretching motions of Ar₂-Ne complex can be expressed by the Hamiltonian [20]:

$$\hat{H} = \hat{K}_V + \hat{K}_{VR} + V(R, r, \theta) \quad (1)$$

$$\hat{K}_V = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R - \frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} r +$$

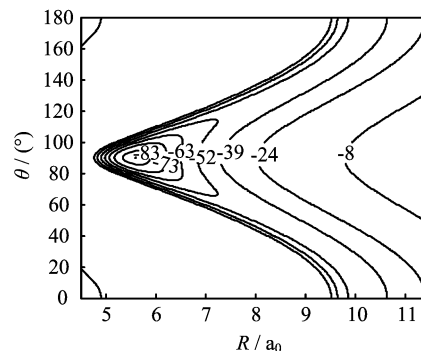


FIG. 1 Contours of PES at $r=7.127$ a₀ for Ar₂-Ne complex (in cm⁻¹).

$$\frac{\hbar^2}{2} \left(\frac{1}{\mu R^2} + \frac{1}{mr^2} \right) \hat{j}^2 \quad (2)$$

$$\hat{K}_{VR} = \frac{1}{2\mu R^2} (\hat{J}^2 - 2\hat{J}_z^2 - \hat{J}_+ \hat{j}_- - \hat{J}_- \hat{j}_+) \quad (3)$$

where μ and m is the reduced mass of complex and monomer Ar₂ respectively, J is the total angular momentum, \hat{J}_\pm, \hat{j}_\pm are the well-known step up/down operators. \hat{K}_{VR} is the Coriolis coupling term describing the interaction of vibration and rotation. \hat{j} is the angular momentum operator of the Ar₂ molecule. The meaning of other variables and symbols can be inspected in Refs.[18, 19].

The rovibrational wave functions are expanded into a basis set

$$\Phi_i^{JMP}(R, r, \theta, \varphi, \alpha, \beta) = \frac{1}{R} \frac{1}{r} \left(\frac{2J+1}{4\pi} \right)^{1/2} \cdot$$

$$\sum_{q_1=0}^{q_1 \max} \sum_{q_2=0}^{q_2 \max} \sum_{j=0}^{j \max} \sum_{k=0}^{\min(j, J)} c_{q_1 q_2 j k}^{J p i} \chi_{q_1}(R) \chi_{q_2}(r) \cdot$$

$$\Phi_{jk}^{JMP}(\theta, \varphi, \alpha, \beta) \quad (4)$$

where α, β are Euler angles, φ, θ describe the orientation of vector r , q_1, q_2 are vibrational quantum numbers for R and r degree of freedom, k is the projection of j onto the z axis in the molecular frame. $\chi_{q_1}(R)$ and $\chi_{q_2}(r)$ are two different stretching basis functions. The angular basis functions are parity-adapted basis function as

$$\Phi_{jk}^{JMP}(\theta, \varphi, \alpha, \beta) = N_k [D_{MK}^{J*}(\alpha, \beta, 0) Y_{jk}(\theta, \varphi) + p(-1)^J D_{M-k}^{J*}(\alpha, \beta, 0) Y_{j-k}(\theta, \varphi)] \quad (5)$$

where $p=\pm 1$ for the total parity of the wavefunction, M is the projection of the total angular momentum J , D_{MK}^{J*} is a Wigner rotation matrix element, Y_{jk} is a spherical harmonic. The normalization factor N_k is $1/2$ for $k=0$ and $1/\sqrt{2}$ for other. The sum over k starts from 1 when $p(-1)^J$ is -1 , otherwise, it begins with $k=0$.

TABLE I Calculated bound state levels E (in cm⁻¹) using the 3D PES of Ar₂-Ne complex.

J_{K_a, K_c}	$E(\text{Ar}_2\text{-}^{20}\text{Ne})$	$E(\text{Ar}_2\text{-}^{22}\text{Ne})$
0 ₀₀	0	0
1 ₁₁	0.149104	0.140402
2 ₀₂	0.281605	0.277715
2 ₁₁	0.380345	0.371628
2 ₂₀	0.545920	0.515008
3 ₁₃	0.573060	0.556775
3 ₂₂	0.827360	0.792568
3 ₃₁	1.148269	1.077646
4 ₀₄	0.895299	0.875956
4 ₁₃	1.103699	1.087570
5 ₁₅	1.318458	1.285688

The quantum number of j should be even required by the exchange symmetry of the complex.

There are a number of choices for the stretching basis function $\chi_{q_1}(R)$ and $\chi_{q_2}(r)$. In this work, the two radial basis functions have been determined as numerical eigensolutions to the two one-dimensional vibrational Schrödinger equations,

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V(R, r_e, \theta_e) \right] \chi_{q_1}(R) = E_{q_1} \chi_{q_1}(R) \quad (6)$$

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V_{\text{Ar}_2}(r) \right] \chi_{q_2}(r) = E_{q_2} \chi_{q_2}(r) \quad (7)$$

where $V(R, r_e, \theta_e)$ is a cut of the Ar₂-Ne interaction potential with Ar₂ frozen at its equilibrium distance r_e and $\theta_e = 90^\circ$. $V_{\text{Ar}_2}(r)$ is the interaction potential of the Ar₂ dimer [8]. The explicit form of the resulting secular Hamiltonian matrix can be written as

$$\begin{aligned} H_{q_1 q_2 j k, q'_1 q'_2 j' k'} &= \delta_{q_1 q'_1} \delta_{q_2 q'_2} \delta_{j j'} \delta_{k k'} (E_{q_1} + E_{q_2}) + \\ &\delta_{q_2 q'_2} \left\langle \chi_{q_1} \left| \frac{\hbar^2}{2\mu R^2} \right| \chi_{q'_1} \right\rangle \left\langle \Phi_{jk}^{JMP} \left| (\hat{J} - \hat{j})^2 \right| \Phi_{j'k'}^{JMP} \right\rangle + \\ &j(j+1) \delta_{q_1 q'_1} \left\langle \chi_{q_2} \left| \frac{\hbar^2}{2\mu r^2} \right| \chi_{q'_2} \right\rangle + \\ &\sum \left\{ \left\langle \chi_{q_1} \chi_{q_2} \left| V_\lambda(r, R) - V(r_e, R, \theta_e) \right| \chi_{q_1} \chi_{q'_2} \right\rangle \cdot \right. \\ &\left. \left\langle \Phi_{jk}^{JMP} \left| P_\lambda(\cos \theta) \right| \Phi_{j'k'}^{JMP} \right\rangle \right\} \end{aligned} \quad (8)$$

where V_λ is the Legendre polynomials expansion coefficient of the potential $V(R, r, \theta)$.

III. RESULTS AND DISCUSSION

A self-written FORTRAN code is used to calculate the rovibrational energy levels and wave functions of the Ar₂-²⁰Ne and Ar₂-²²Ne isotopomers. The energy

TABLE II Observed and calculated rotational transitions of the Ar₂-²⁰Ne complex in its ground vibrational state (in cm⁻¹).

J_{K_a, K_c} $J'_{K'_a, K'_c}$	Exp. [8]	Cal.	Error	
			Absolute	Relative/%
1 ₁₁ -0 ₀₀	0.1514	0.1491	0.0023	1.5362
2 ₂₀ -2 ₁₁	0.1708	0.1676	0.0032	1.4662
2 ₂₀ -1 ₁₁	0.4029	0.3968	0.0060	1.5009
2 ₀₂ -1 ₁₁	0.1319	0.1325	-0.0006	-0.4455
3 ₃₁ -3 ₂₂	0.3295	0.3239	0.0056	1.6161
3 ₂₂ -3 ₁₃	0.2591	0.2543	0.0048	1.8506
3 ₃₁ -2 ₂₀	0.6127	0.6023	0.0104	1.6919
3 ₁₃ -2 ₀₂	0.2951	0.2915	0.0036	1.2150
3 ₂₂ -2 ₁₁	0.4540	0.4470	0.0070	1.5381
4 ₁₃ -4 ₀₄	0.2085	0.2084	0.0001	0.0611
4 ₀₄ -3 ₁₃	0.3238	0.3222	0.0016	0.4854
4 ₁₃ -3 ₂₂	0.2732	0.2763	-0.0030	-1.1330
5 ₁₅ -4 ₀₄	0.4275	0.4232	0.0043	1.0052

TABLE III Observed and calculated rotational transitions of the Ar₂-²²Ne complex in its ground vibrational state (in cm⁻¹).

J_{K_a, K_c} $J'_{K'_a, K'_c}$	Exp. [8]	Cal.	Error	
			Absolute	Relative/%
1 ₁₁ -0 ₀₀	0.1426	0.1404	0.0022	1.5189
2 ₂₀ -2 ₁₁	0.1481	0.1454	0.0027	1.6848
2 ₂₀ -1 ₁₁	0.3801	0.3746	0.0055	1.4557
2 ₀₂ -1 ₁₁	0.1369	0.1373	-0.0004	-0.2830
3 ₃₁ -3 ₂₂	0.2929	0.2871	0.0058	1.5654
3 ₂₂ -3 ₁₃	0.2401	0.2358	0.0043	1.7938
3 ₃₁ -2 ₂₀	0.5722	0.5626	0.0096	1.6760
3 ₁₃ -2 ₀₂	0.2825	0.2791	0.0034	1.2031
3 ₂₂ -2 ₁₁	0.4274	0.4209	0.0065	1.5208
4 ₁₃ -4 ₀₄	0.2116	0.2116	0.0001	0.0145
4 ₀₄ -3 ₁₃	0.3210	0.3192	0.0019	0.5806
4 ₁₃ -3 ₂₂	0.2926	0.2950	-0.0020	-0.8240
5 ₁₅ -4 ₀₄	0.4138	0.4097	0.0041	0.9830

levels for $J \leq 5$ in ground vibrational state are presented in Table I.

The nuclei ⁴⁰Ar is zero spin particles and obeys Bose-Einstein statistics. The Ar₂-Ne trimer has C_{2v} symmetry with the b axis as the symmetry axis. An exchange of two identical bosons through a C₂ operation requires that the total wave function of the system is symmetric with respect to this operation. Because of the zero spin of the Ar nuclei, only symmetric spin wave functions exist. Thus, only levels with symmetric rotational wavefunctions ($K_a, K_c = o, o$ and e, e) exist. Half of the energy levels, *i.e.* those with asymmetric rotational wavefunctions ($K_a, K_c = o, e$ and o, e) are therefore missed in the Ar₂-Ne trimer as indicated in Table I.

The principal a-inertia axis lies parallel to the Ar-Ar

TABLE IV Spectroscopic constants of Ar₂-Ne (in MHz).

	Ar ₂ - ²⁰ Ne		Ar ₂ - ²² Ne	
	Exp. [8]	This work	Exp. [8]	This work
<i>A</i>	3402.7684	3342.0006	3165.1123	3109.2072
ΔA	237.6564	232.7934		
<i>B</i>	1739.7172	1733.1084	1739.6328	1732.9947
ΔB	0.0844	0.1137		
<i>C</i>	1137.2952	1128.0111	1109.2292	1099.9451
ΔC	28.0660	29.0660		

unit and the *b*-inertia axis is perpendicular to Ar-Ar unit. Therefore Ar₂-Ne has a nonvanishing dipole moment only along the *b* axis, leading to *b*-type transitions. The transitions selective rules are $\Delta K_a = \pm 1$ and $\Delta K_c = \pm 1$. Table II and Table III present the results of Ar₂-²⁰Ne and Ar₂-²²Ne along with the experimental data respectively. It can be seen that our theoretical results are in good agreement with the experiments. The theoretical results are slightly bigger than the experimental data in general. The relative error is within 2%.

Table IV shows the comparison of the calculated rotational constants *A*, *B*, *C* and ΔA , ΔB , ΔC with experimental results of the constants. ΔA , ΔB , ΔC are the isotope shifts of the Ar₂-²²Ne values with respect to that of the Ar₂-²⁰Ne complex. The theoretical results of *B* and *C* parameters calculated from our potential agree very well with their experimental counterparts. There is a slight underestimation about 1.9% of the rotational constant *A*. *A* depends mostly on the equilibrium distance from Ne atom and the mass center of Ar₂ dimer (depends on the Ne-Ar interaction, in other words). The discrepancy of *A* is probably due to an inadequacy of aug-cc-pVQZ basis set for Ne atom which is also found in other works. The largest isotopic shift among the three rotational constants is in *A* as expected. Because *b* inertial axis lies roughly vertical to the Ar-Ar vector, the *B* depends mostly on the Ar-Ar interaction and ΔB is very small. And *C* is more sensitive to the Ar-Ar interaction than to the Ar-Ne interaction.

IV. CONCLUSION

The *ab initio* calculation of three-dimensional PES for the Ar₂-Ne complex is performed by CCSD(T) method and avqz+33221 basis set. A total of 1288 configurations are included in the calculation. The three-dimensional PES is constructed via a two-step procedure. Based on the fitted three-dimensional PES, the rovibrational bound states calculation is implemented including the Coriolis coupling terms. The theoretical spectroscopic constants and transition frequencies in the van der Waals ground vibrational state are in good agreement with the experimental results.

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- [1] W. Jäger, Y. Xu, and M. C. L. Gerry, *J. Chem. Phys.* **99**, 919 (1993).
- [2] Y. Xu, W. Jäger, J. Djauhari, and M. C. L. Gerry, *J. Chem. Phys.* **103**, 2827 (1995).
- [3] S. M. Cybulski and R. R. Toczyłowski, *J. Chem. Phys.* **111**, 10520 (1999).
- [4] J. L. Cacheiro, B. Fernández, D. Marchesan, S. Coriani, C. Hättig, and A. Rizzo, *Mol. Phys.* **102**, 101 (2004).
- [5] S. M. Cybulski and R. R. Toczyłowski, *J. Chem. Phys.* **119**, 5487 (2003).
- [6] Y. Xu, W. Jäger, and M. C. L. Gerry, *J. Chem. Phys.* **100**, 4171 (1994).
- [7] A. Ernesti and J. M. Hutson, *J. Chem. Phys.* **103**, 3386 (1995).
- [8] Y. Xu, and W. Jäger, *J. Chem. Phys.* **107**, 4788(1997).
- [9] S. Orlandini, I. Baccarelli, and F. A. Gianturcoa, *Comput. Phys. Comm.* **180**, 384 (2009).
- [10] H. L. Han, Y. Li, X. Z. Zhang, and T. Y. Shi, *J. Chem. Phys.* **127**, 154104 (2007).
- [11] T. B. Pedersen, J. L. Cacheiro, B. Fernández, and H. Koch, *J. Chem. Phys.* **117**, 6562 (2002).
- [12] Z. Q. Wang, M. Y. Gong, Y. Zhang, E. Y. Feng, and Z. F. Cui, *Chem. Phys. Lett.* **454**, 7 (2008).
- [13] E. Y. Feng, Y. Zhang, Z. Q. Wang, M. Niu, and Z. F. Cui, *J. Chem. Phys.* **130**, 124311 (2009).
- [14] T. H. Dunning Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- [15] S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- [16] H. J. Werner, P. J. Knowles, F. R. Manby, M. Schtz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, MOLPRO, version 2006.1.
- [17] R. Bukowski, J. Sadlej, B. Jeziorski, P. Jankowski, K. Szalewicz, S. A. Kucharski, H. L. Williams, and B. M. Rice, *J. Chem. Phys.* **110**, 3785 (1999).
- [18] E. Y. Feng, Z. Q. Wang, M. Y. Gong, and Z. F. Cui, *J. Chem. Phys.* **127**, 174301 (2007).
- [19] Z. Q. Wang, M. Y. Gong, Y. Zhang, E. Y. Feng, and Z. F. Cui, *J. Chem. Phys.* **128**, 044309 (2008).
- [20] Y. Guan and J. T. Muckerman, *J. Phys. Chem.* **95**, 8293 (1991).