A new *ab initio* potential energy surface for the NeCO complex with the vibrational coordinate dependence

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A new high quality three-dimensional potential energy surface for the Ne–CO van der Waals complex is developed using the CCSD(T) method and avqz/avqz+33221 basis set. The *ab initio* calculation is performed in a total of 1365 configurations with supermolecule method. There is a single global minimum located in a nearly T-shaped geometry. The global minimum energy is -49.4090 cm^{-1} at $R_e = 6.40a_0$ and $\theta_e = 82.5^\circ$ for V_{00} . Using the three-dimensional potential energy surface, we have calculated bound rovibrational energy levels up to $J = 10$ including the Coriolis coupling terms. Compared with the experimental transition frequencies, the theoretical results are in good agreement with the experimental results. © 2011 American Institute of Physics. [doi:10.1063/1.3517313]

I. INTRODUCTION

The triatomic complexes Rg–CO (Rg = He, Ne, Ar, Kr, Xe) are the simplest weakly bound cluster and make up an interesting family with small binding energies and rotational structure determined by the hindered internal rotation of the CO subunit.

Experimentally, all the Rg–CO complexes have been studied.^{1–9} In 1994, Chuaqui *et al.*¹ reported high-resolution infrared spectra near the fundamental band region of the CO monomer for the complex with ³He and ⁴He. Chan *et al.*² applied a more powerful spectroscopic technique to detect the “hidden” lines in the spectra of the He–CO, which were obscured by transitions of CO monomer in the original measurements in 1996. McKellar and Chan³ reported the infrared absorption spectra of the Ne–CO complex in 1998. Walker *et al.*⁴ measured the pure rotational spectra of the Ne–CO complex, using a pulsed jet and cavity microwave Fourier transform spectrometer in 1997. In 1993, Randall *et al.*⁵ reported an experimental study of the infrared spectrum of Ne–CO corresponding to the simultaneous excitation of vibration and internal rotation of the CO subunit within the complex.

The first experimental study of infrared spectrum for the Ar–CO complex was reported by McKellar *et al.*⁶ in 1992. They assigned six *b*-type transitions (with $\Delta K = \pm 1$) for K values up to three in the CO fundamental band. In 1996, Xu *et al.*⁷ extended this work to K values up to six. For the Kr–CO and Xe–CO complexes, McKellar⁸ observed the infrared spectra in 1993. Walker *et al.*⁴ measured the pure rotational spectra, using a pulsed jet and cavity microwave Fourier transform spectrometer in 1997. In 1998, Brookes and McKellar⁹ also recorded the infrared spectra of both the complexes. In 2001, millimeter-wave spectroscopy of the Kr–CO and Xe–CO complexes was reported by Walker and McKellar¹⁰ using a coaxial jet spectrometer.

On the theoretical^{11–16} side, a lot of attentions were attracted on the Rg–CO complexes. For instance, in 2005, Peterson and McBane¹¹ constructed the three-dimensional PES of the He–CO complex. They employed the CCSD(T) method and extrapolated the individual counterpoise-corrected interaction energy to complete basis set limit. They also used the CCSDT method in order to investigate the small intrinsic error in the CCSD(T) method itself. Compared with experiment, the results based on the CCSDT potential exhibited the root-mean-square (rms) error and maximum errors just of 0.03 and 0.04 cm^{-1} , respectively. In 1997, Heijmen *et al.*¹² used the three-dimensional symmetry-adapted perturbation theory (SAPT) potential to calculate the bound state of the He–CO complex. The computed *ab initio* transition frequencies were found to agree within 0.1 cm^{-1} with experiment. Moszynski *et al.*¹³ reported the three-dimensional potential energy surface (PES) of the Ne–CO complex in 1997. The theoretical results were in agreement with the experimental data. This potential was not perfect and required small scalings to reproduce the experimental data. In 2002, Pedersen and Koch¹⁴ employed the CCSD(T) method and aug-cc-pVQZ basis set extended with a (3s3p2d1f1g) set of midbond functions to calculate the three-dimensional PES of the Ar–CO complex. When compared the results with available experimental data, 650 observed transitions were reproduced with rms error of 0.13 cm^{-1} . In our recent work, we presented a two-dimensional PES for the Kr–CO (Ref. 15) and Xe–CO complexes.¹⁶ Bound state energies were calculated up to $J = 12$. The predicted transition frequencies and spectroscopic constants were in good agreement with the experimental results.

In this paper, we report the calculations of the three-dimensional potential energy surface and bound states of the Ne–CO complex. The plan of this paper is as follows. In Sec. II, the *ab initio* calculations of the interaction potential energy are briefly described and the analytical fits of the computed energies in configurations are presented. In Sec. III, the method used for the calculation of the bound states and the

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theoretical results are presented. The comparison of predicted transition frequencies and spectroscopic constants with the experimental results is also given in this section. Finally, in Sec. IV we present the conclusions.

II. POTENTIAL ENERGY SURFACE

A. *Ab initio* calculation

Jacobi coordinates are used throughout the present work. In these coordinates, r_{CO} is the CO bond length, R refers to the distance between the Ne atom and the center of mass of CO molecule, and θ is the angle between R and r_{CO} with $\theta = 0^\circ$ referring to the Ne–C–O linear configuration.

The Ne–CO interaction potential was calculated by the singles and doubles level of theory with a perturbative treatment of connected triple excitations [CCSD(T)] and using correlation-consistent basis sets augmented with an additional set of midbond function. As for the basis set we employ the aug-cc-pVQZ basis set for the Ne, O, and C atoms. Midbond functions (3s3p2d2f1g) (for 3s and 3p, $\alpha = 0.9, 0.3$, and 0.1 ; for 2d and 2f, $\alpha = 0.6$ and 0.2 ; and for 1g, $\alpha = 0.3$) are used to eliminate the need for higher angular momentum functions in the atom-centered basis set. The supermolecule approach is employed to get the intermolecular potential energy. The counterpoise procedure of Boys and Bernardi is adopted to correct for the basis set superposition error (BSSE).¹⁷

In summary, the PES of the Ne–CO complex is calculated at the CCSD(T) level with avqz/avqz+33221 basis set. Calculations are carried out for five values of the CO bond length r_{CO} : $\{1.9, 2.0, 2.132, 2.2, 2.4\}a_0$, 21 values of the intermolecular separation R : $\{5.0, 5.5, 6.0, 6.2, 6.5, 6.8, 7.0, 7.2, 7.5, 7.8, 8.0, 8.5, 9.0, 9.5, 10, 11, 12, 13, 14, 15, 16\}a_0$, and 13 angles θ : $\{0, 20, 40, 60, 80, 90, 105, 115, 125, 135, 150, 165, 180\}^\circ$, resulting in the potential energy surface consisting of a total of 1365 configurations. The calculations have been performed with MOLPRO 2006 package.¹⁸

B. Fitting procedure

The complete three-dimensional PES $V(r, R, \theta)$ is constructed by two steps. First, we construct five two-dimensional PESs at values of $r_{\text{CO}} = \{1.8, 1.9, 2.132, 2.2, 2.6\}a_0$ using the potential model proposed by Bukowski *et al.*¹⁹ The two-dimensional potential model contains short range V_{sh} and asymptotic V_{as} contributions,

$$V(R, \theta) = V_{\text{sh}}(R, \theta) + V_{\text{as}}(R, \theta). \quad (1)$$

Here,

$$V_{\text{sh}} = G(R, \theta)e^{B(\theta)-D(\theta)R}, \quad (2)$$

$$V_{\text{as}}(R, \theta) = \sum_{n=6}^9 \sum_{\substack{l=0,2,\dots \\ l=1,3,\dots}}^{n-4} f_n(D(\theta)R) \frac{C_{nl}}{R^n} P_l^0(\cos \theta), \quad (3)$$

where $D(\theta)$, $B(\theta)$, and $G(R, \theta)$ are all expansions in Legendre polynomials $P_\ell(\cos \theta)$:

$$B(\theta) = \sum_{l=0}^5 b_l P_l^0(\cos \theta), \quad (4)$$

$$D(\theta) = \sum_{l=0}^5 d_l P_l^0(\cos \theta), \quad (5)$$

$$G(R, \theta) = \sum_{l=0}^5 (g_{0l} + g_{1l}R + g_{2l}R^2 + g_{3l}R^3) P_l^0(\cos \theta). \quad (6)$$

The $f_n(x)$ is the Tang–Toennies damping function.²⁰ In order to obtain the most reliable fit, in particular, for the long-range part of the potential, we follow a two-step linear least squares fit procedure.^{15,16} Those configurations with energy more than 500 cm^{-1} are excluded from the fit.

Second, we use the five two-dimensional PESs to construct the three-dimensional PES by interpolating along $(r - r_e)$ using a fourth-order polynomial,²¹

$$V(r, R_j, \theta_k) = a_0 + a_1(r - r_e) + a_2(r - r_e)^2 + a_3(r - r_e)^3 + a_4(r - r_e)^4 \quad (7)$$

where a_i can be solved using the matrix equation,

$$\begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 1 & r_1 - r_e & (r_1 - r_e)^2 & (r_1 - r_e)^3 & (r_1 - r_e)^4 \\ 1 & r_2 - r_e & (r_2 - r_e)^2 & (r_2 - r_e)^3 & (r_2 - r_e)^4 \\ 1 & r_3 - r_e & (r_3 - r_e)^2 & (r_3 - r_e)^3 & (r_3 - r_e)^4 \\ 1 & r_4 - r_e & (r_4 - r_e)^2 & (r_4 - r_e)^3 & (r_4 - r_e)^4 \\ 1 & r_5 - r_e & (r_5 - r_e)^2 & (r_5 - r_e)^3 & (r_5 - r_e)^4 \end{pmatrix}^{-1} \times \begin{pmatrix} V(r_1, R_j, \theta_k) \\ V(r_2, R_j, \theta_k) \\ V(r_3, R_j, \theta_k) \\ V(r_4, R_j, \theta_k) \\ V(r_5, R_j, \theta_k) \end{pmatrix}. \quad (8)$$

Here, r_i corresponds to $r_{\text{CO}} = \{1.9, 2.0, 2.132, 2.2, 2.4\}a_0$, respectively, and $r_e = 2.132a_0$.

The total rms error is 0.026 cm^{-1} and the maximum absolute deviation is 0.12 cm^{-1} for 1365 fitting configurations. In order to test the accuracy, we compare the interaction energies predicted by our three-dimensional PES with the *ab initio* values calculated at $r_{\text{CO}} = 2.3a_0$ in a total of 273 configurations. The total test rms error is 0.34 cm^{-1} and the maximum absolute deviation is 0.15 cm^{-1} . The comparisons are listed in Table I. We see that our PES agrees well with the *ab initio*

TABLE I. Comparison of our three-dimensional surface with *ab initio* CCSD(T) computations. The Δ_{max} is the maximum absolute deviation, and the Δ_{rms} is the root-mean-square deviation. All the deviations are reported in cm^{-1} .

Energy range (cm^{-1})	Fitting points			Testing points		
	No. of points	Δ_{max}	Δ_{rms}	No. of points	Δ_{max}	Δ_{rms}
500–0	125	0.06	0.025	25	0.12	0.035
–20–0	660	0.07	0.028	132	0.11	0.033
<–20	240	0.06	0.022	48	0.11	0.034

FIG. 1. Contour plot of the V_{00} potential energy surface for the Ne-CO complex (in cm^{-1}).

calculation, indicating that our surface is a faithful representation of the CCSD(T) potential energy.

Once the five two-dimensional potentials are determined, the vibrationally adiabatic potential can be constructed. Some previous works^{11,14} showed that the vibrationally adiabatic potential provides a good explanation for the experiment results. The vibrationally averaged Ne-CO potential can be expressed as²¹

$$V_{vv}(R, \theta) = \langle \chi_v(r) | V(r, R, \theta) | \chi_v(r) \rangle, \quad (9)$$

in which the CO vibrational eigenfunctions $\chi_v(r)$ are determined from the potential curve $V_{\text{CO}}(r)$ for zero angular momentum. The empirical potential curve of Huxley and Murrell²² (with $r_e = 2.132a_0$) have been used to calculate $\chi_v(r)$.

C. Features of the surface

Figure 1 plots contours of the V_{00} surface. There is a single global minimum located in a nearly T-shaped geometry. The global minimum energy is -49.4090 cm^{-1} at $R_e = 6.40a_0$ and $\theta_e = 82.5^\circ$. The linear Ne-C-O geometry is lower in energy (-43.2824 cm^{-1} at $R = 7.00a_0$) than the linear Ne-O-C geometry (-31.2998 cm^{-1} at $R = 8.10a_0$). The potential is rather flat, making possible large amplitude motions. Contour plots of the V_{11} and V_{22} surfaces show the same overall features, although they have slightly deeper minima.

III. ROVIBRATIONAL ENERGY LEVELS CALCULATION

A. Computational details

The Hamiltonian can then be expressed as²³

$$H = -\frac{\hbar^2}{2mR} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2mR^2} (\hat{J} - \hat{j})^2 + b_v \hat{j}^2 + V_{vv'}(R, \theta) \quad (10)$$

with

$$(\hat{J} - \hat{j})^2 = \hat{J}^2 + \hat{j}^2 - 2\hat{j}_z \hat{J}_z - \hat{j}_+ \hat{J}_- - \hat{j}_- \hat{J}_+, \quad (11)$$

where $\hat{J}$ denotes the total angular momentum operator of the Ne-CO complex, $\hat{j}$ means the angular momentum operator of rigid CO molecule and b_v its rotational constant, m is the reduced mass of the complex, and $V(R, \theta)$ is the Ne-CO interaction potential. Finally, $\hat{j}_\pm$ stands for $\hat{j}_x \pm i\hat{j}_y$ and $\hat{J}_\pm$ for $\hat{J}_x \pm i\hat{J}_y$.

Using the body-fixed coordinate system in which the z axis is attached to R , the nuclear Schrödinger equation may be written as

$$H \psi_i^{JMp}(R, \theta, \varphi, \alpha, \beta) = E_i^{Jp} \psi_i^{JMp}(R, \theta, \varphi, \alpha, \beta). \quad (12)$$

The eigensolutions are labeled by good quantum numbers as J for the total angular momentum of the Ne-CO complex and M for the magnetic quantum number, $p = \pm 1$ for the total parity of the wavefunction. The index i is a state label for the different energy levels with a given set of J, M, p .

To solve the Schrödinger equation, first the potential $V(R, \theta)$ is expanded into Legendre polynomials as

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{\max}} V_\lambda(R) P_\lambda^0(\cos \theta). \quad (13)$$

Then, the wave functions are expanded into a basis set,

$$\begin{aligned} \psi_i^{JMp}(R, \theta, \varphi, \alpha, \beta) &= \frac{1}{R} \left(\frac{2J+1}{4\pi} \right)^{1/2} \\ &\times \sum_{q=0}^{q_{\max}} \sum_{j=0}^{j_{\max}} \sum_{k=0 \text{ or } 1}^{\min(j, J)} c_{q,jk}^{Jpi} \chi_q(R) \Phi_{jk}^{JMp}(\theta, \varphi, \alpha, \beta), \end{aligned} \quad (14)$$

where $\chi_q(R)$ is the stretching basis function. The angular basis functions are parity-adapted basis function as

$$\begin{aligned} \Phi_{jk}^{JMp}(\theta, \varphi, \alpha, \beta) &= N_k [D_{Mk}^{J*}(\alpha, \beta, 0) Y_{jk}(\theta, \varphi) \\ &+ p(-1)^J D_{M-k}^{J*}(\alpha, \beta, 0) Y_{j-k}(\theta, \varphi)]. \end{aligned} \quad (15)$$

Here, D_{MK}^{J*} is an element of a Wigner rotation matrix and Y_{jk} a spherical harmonic. The normalization factor N_k is $1/2$, for $k = 0$, and $1/\sqrt{2}$, else. The sum over k starts from 1 when $p(-1)^J$ is -1 , otherwise it begins with $k = 0$.

There are a number of choices for the stretching basis function $\chi_q(R)$: harmonic oscillator eigenfunctions, Morse potential eigenfunctions, or other basis function tailored from the potential.²³ In this work, the radial basis functions have been determined as numerical eigensolutions to the vibrational Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + V(R, 82.5^\circ) \right] \chi_q(R) = E_q \chi_q(R), \quad (16)$$

where $V(R, 82.5^\circ)$ is a cut of the Ne-CO interaction potential at an angle of 82.5° . This choice has two advantages: simplifying the interpretation of the wave function and

TABLE II. Transitions in the $K = 2 \leftarrow 1$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	$Q[f \leftarrow e](J)$	$Q[e \leftarrow f](J)$	$R[e \leftarrow e](J)$	$R[f \leftarrow f](J)$
1			2150.5556 0.0030	2150.5415 0.0032
2	2150.1429 0.0067	2150.0984 0.0065	2150.7565 0.0022	2150.7156 0.0006
3	2150.1405 0.0061	2150.0496 0.0083	2150.9514 −0.0015	2150.8734 −0.0011
4	2150.1371 0.0055	2149.9810 0.0063	2151.1355 −0.0080	2151.0143 −0.00424
5	2150.1327 0.0046	2149.8883 0.00267	2151.3016 −0.0160	2151.1381 −0.0055
6	2150.1272 0.0036	2149.7646 −0.0023	2151.4379 −0.0268	2151.2441 −0.0089
7	2150.1205 0.0021	2149.5985 −0.0111	2151.5287 −0.0414	2151.3318 −0.0112
8	2150.1125 0.0007	2149.3746 −0.0250	2151.5570 −0.0626	2151.4004 −0.0146
9	2150.1031 −0.0007	2149.0761 −0.0435	2151.5114 −0.0862	2151.4490 −0.0184

minimizing the required $q_{\max}$. When $\chi_q(R)$'s have been obtained, the Hamiltonian matrix can be given as

$$\begin{aligned}
 H_{qjk,q'j'k'} &= \delta_{qq'}\delta_{jj'}\delta_{kk'}[E_q + b_v j(j+1)] \\
 &+ \langle \chi_q | \frac{\hbar^2}{2mR^2} | \chi_{q'} \rangle \langle \Phi_{jk}^{JMp} | (\hat{J} - \hat{j})^2 | \Phi_{j'k'}^{JMp} \rangle \\
 &+ \sum_{\lambda} \langle \chi_q | V_{\lambda}(R) - V_{\lambda}(R, 82.5^\circ) | \chi_{q'} \rangle \\
 &\times \langle \Phi_{jk}^{JMp} | P_{\lambda}^0(\cos \theta) | \Phi_{j'k'}^{JMp} \rangle.
 \end{aligned} \quad (17)$$

TABLE III. Transitions in the $K = 1 \leftarrow 2$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	$Q[e \leftarrow f](J)$	$Q[f \leftarrow e](J)$	$P[e \leftarrow e](J)$	$P[f \leftarrow f](J)$
2	2136.0608 −0.0712	2136.1056 −0.0726	2135.6488 −0.0685	2135.6630 −0.0685
3	2136.0615 −0.0709	2136.2628 0.0381	2135.4465 −0.0668	2135.4876 −0.0659
4	2136.0626 −0.0703	2136.2200 −0.0699	2135.2498 −0.0628	2135.3282 −0.0646
5	2136.0642 −0.0697	2136.3108 −0.0665	2135.0636 −0.0577	2135.1851 −0.0621
6	2136.0664 −0.0675	2136.4329 −0.0609	2134.8956 −0.0498	2135.0588 −0.0594
7	2136.0694 −0.0671	2136.5977 −0.0523	2134.7577 −0.0377	2134.9499 −0.0563
8	2136.0735 −0.0658	2136.8214 −0.0378	2134.6663 −0.0206	2134.8590 −0.0531
9	2136.0788 −0.0632	2137.1207 −0.0177	2134.6387 0.0016	2134.7869 −0.0500

TABLE IV. Transitions in the $K = 3 \leftarrow 2$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	$Q[f \leftarrow e](J)$	$Q[e \leftarrow f](J)$	$R[e \leftarrow e](J)$	$R[f \leftarrow f](J)$
3	2153.7329 0.0099			
4	2153.7077 −0.0066			
5	2153.6905 −0.0162			2154.8572 −0.0454
6	2153.6886 −0.0257		2155.0954 −0.1517	2155.0202 −0.0594
7	2153.7115 −0.0295	2153.4691 −0.1476	2155.2919 −0.1340	2155.1742 −0.0744
8	2153.7710 −0.0285	2153.5532 −0.1349	2155.5035 −0.1147	2155.3130 −0.0901
9	2153.8781 −0.0245	2153.4691 −0.1274		

In the above expression, the required matrix elements of $P_{\lambda}^0(\cos \theta)$ and $(\hat{J} - \hat{j})^2$ over angular basis functions $\Phi_{jk}^{JMp}(\theta, \varphi, \alpha, \beta)$ can be calculated by standard angular momentum coupling method. When the discrete variable representation method is used to solve the Eq. (16) the integral over R can be simply given by²³

$$\langle \chi_q | g(R) | \chi_{q'} \rangle \cong \sum_{i=1}^N \chi_q(R_i) g(R_i) \chi_{q'}(R_i), \quad (18)$$

where R_i is the i th grid-point value of R . After the Hamiltonian matrix is set up in terms of the basis functions, the rovibrational energies and the expanded coefficients $c_{q,jk}^{J,pi}$ are obtained from solution of the corresponding secular equation.

TABLE V. Transitions in the $K = 2 \leftarrow 3$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	$Q[e \leftarrow f](J)$	$Q[f \leftarrow e](J)$	$P[e \leftarrow e](J)$	$P[f \leftarrow f](J)$
3	2132.3003 −0.0661			
4	2132.3227 −0.0535		2131.5058 −0.0555	
5	2132.3415 −0.0473	2132.3600 0.0194	2131.3268 −0.0510	2131.3430 0.0450
6	2132.3462 −0.0418	2132.3944 0.0293	2131.1447 −0.0551	2131.1773 0.0675
7	2132.3276 −0.0374	2132.4383 0.0322	2130.9588 −0.0666	2131.0169 0.0954
8	2132.2741 −0.0368	2132.4982 0.0345	2130.7650 0.0573	2130.8659 0.1344
9	2132.1749 −0.0405	2132.5834 0.0382	2130.5577 −0.0200	2130.7306 0.2001

TABLE VI. Transitions in subbands involving the first excited bending state, $v_2 = 1$, of Ne–CO (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	$Q(1,1) \leftarrow (1,0)$	$Q(1,1) \leftarrow (0,1)$	$R(0,0) \leftarrow (1,0)$	$P(0,0) \leftarrow (1,0)$
0			2134.8708 0.0343	
1	2149.6525 0.0096	2136.4747 –0.0662	2135.0912 0.0319	2134.4458 0.0376
2	2149.6611 0.0091	2136.4666 –0.0649	2135.3167 0.0291	2134.2421 0.0386
3	2149.6739 0.0086	2136.4546 –0.0646	2135.5471 0.0257	2134.0449 0.0389
4	2149.6905 0.0079	2136.4389 –0.0635	2135.7825 0.0211	2133.8548 0.0387
5	2149.7108 0.0065	2136.4200 –0.06172	2136.0228 0.0157	2133.6726 0.0374
6	2149.7340 0.0043	2136.3984 –0.0589	2136.2682 0.0107	2133.4991 0.0356
7	2149.7594 0.0014	2136.3750 –0.0556	2136.5188 0.0054	2133.3351 0.03384
8	2149.7856 –0.0022	2136.3514 –0.0519	2136.7749 –0.0021	2133.1816 0.0303
9	2149.8105 –0.0058	2136.3295 –0.0477	2137.0363 –0.0092	2133.0395 0.0265

B. Theoretical results

A self-written Fortran code²³ is used to calculate the rovibrational energy levels and wave functions of the Ne–CO complex. After careful testing we expand potential in Legendre polynomials up to $\lambda_{\text{max}} = 13$. The basis set param-

TABLE VII. Transitions in the $\Sigma \leftarrow \Sigma$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	P		R	
	Ref. 13	This work	Ref. 13	This work
0			2143.4770 0.060	2143.3815 –0.0355
1	2143.0409 0.058	2142.9508 –0.0319	2143.6947 0.061	2143.5962 –0.0375
2	2142.8232 0.058	2142.7353 –0.0299	2143.9118 0.062	2143.8099 –0.0394
3	2142.6061 0.058	2142.5202 –0.0283	2144.1278 0.064	2144.0224 –0.0412
4	2142.3900 0.058	2142.3057 –0.0262	2144.3426 0.066	2144.2334 –0.0434
5	2142.1751 0.059	2142.0922 –0.0241	2144.5556 0.069	2144.4424 –0.0445
6	2141.9620 0.060	2141.8800 –0.0218	2144.7665 0.069	2144.6491 –0.04823
7	2141.7508 0.062	2141.6695 –0.0193	2144.9751 0.073	2144.8533 –0.0487
8	2141.5420 0.063	2141.4611 –0.0180	2145.1807 0.076	2145.0543 –0.0506
9	2141.3360 0.065	2141.2551 –0.0160		

ters j_{max} and q_{max} are 40 and 60, respectively. The rotational constant of CO is $b_0 = 1.92253 \text{ cm}^{-1}$ for $v_{\text{CO}} = 0$ and $b_0 = 1.90502 \text{ cm}^{-1}$ for $v_{\text{CO}} = 1$ from the NIST Standard Reference Database.²⁴ The numerical integration over R is performed with 500 equidistant grids distributed from $5.0a_0$ to $16a_0$.

We calculate the bound state energies for total angular momentum from $J = 0$ to 10. Here, the pair of indices (n_{vdW}, K) is used as a formal replacement of the state label i in Eq. (12). The n_{vdW} represents only the counter of the stretching/bending states. Speaking strictly, K is not a good conserved quantum number due to the additional offdiagonal Coriolis coupling terms, $\hat{J}_+ \hat{J}_-$ and $\hat{J}_- \hat{J}_+$ in Eq. (11). But the calculation shows that the general structure of the level schemes at least for the lower stretching/bending states remains unchanged by relaxing these offdiagonal terms, mainly because of the prefactor whose order of magnitude is about 0.1 cm^{-1} . In addition, we calculate the expectation value $\langle K \rangle$ of the $\hat{J}_z \hat{J}_z$ (or, equivalently, of the $\hat{J}_z \hat{J}_z$ and $\hat{J}_z \hat{J}_z$) as

$$\langle K \rangle = \langle j_z j_z \rangle^{1/2} = \left(\sum_{q,j,k} K^2 C_{qjk}^2 \right)^{1/2}. \quad (19)$$

If $\langle K \rangle$'s are approximation good quantum numbers, they should close to integer numbers. It is indeed close to this situation in most cases.

The energy of a given state is then given by

$$E_{v_{\text{CO}}, v_{\text{vdW}}, K}^{J,p} = E_{v_{\text{CO}}} + \Delta E_{v_{\text{CO}}, v_{\text{vdW}}, K}^{J,p}. \quad (20)$$

Here $E_{v_{\text{CO}}}$ is the CO vibrational energy and $E_{v_{\text{CO}}, v_{\text{vdW}}, K}^{J,p}$ is the van der Waals mode energy. Transition frequencies are then obtained as simple energy differences.

The wave functions of the first four $J = 0$ vibrational levels of V_{00} and V_{11} are presented in left and right columns of Fig. 2. The ground vibrational energy is $E_0 = -31.4531 \text{ cm}^{-1}$, which corresponds to a zero-point energy of 17.9559 cm^{-1} , while for the surface the $E_0 = -31.5325 \text{ cm}^{-1}$ and corresponds to a zero-point energy of 17.8998 cm^{-1} . It can be seen that the contours of these state are mainly localized on the near T-shaped geometry. The first excited vibrational level is -22.9424 cm^{-1} for V_{00}

TABLE VIII. Transitions in the $\Sigma \leftarrow \Sigma^{\text{excited}}$ subband of CO–Ne (all values in cm^{-1}). The theoretical values are positioned on each first line and the (theo.–expt.) values on each second line.

J	P		R	
	Ref. 13	This work	Ref. 13	This work
0			2151.6719 –0.230	2151.8006 –0.1012
1	2151.2380 –0.236	2151.3754 –0.0981	2151.8852 –0.221	2152.0041 –0.1019
2	2151.0181 –0.232	2151.1543 –0.0954		
3	2150.7965 –0.224	2150.9280 –0.0925		
4	2150.5733 –0.212	2150.6965 –0.0889

FIG. 2. Contours of the wave functions for the first four vibrational levels ($J=0$) of Ne-CO complex with $v_{\text{CO}} = 0$ (left column) and $v_{\text{CO}} = 1$ (right column).

surface and -23.1079 cm^{-1} for V_{11} surface, corresponds basically to a bending excitation observed from the node structure. We thus deduce the bending ground frequency is 8.5107 cm^{-1} for $v_{\text{CO}} = 0$ and 8.4246 cm^{-1} for $v_{\text{CO}} = 1$. The second excited level, at -17.8982 cm^{-1} for V_{00} surface and

-18.0244 cm^{-1} for V_{11} surface is already a combination of bending and stretching excitation, as can be seen from the shape of its wavefunction but is still mainly two quanta of bending excitation. The next level, at -10.9846 cm^{-1} for V_{00} surface and -11.0880 cm^{-1} for V_{11} surface, can be assigned

TABLE IX. Spectroscopic constants (in cm^{-1}) of the van der Waals ground state of $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ complex.

	Expt. (Ref. 3) ($\nu_{\text{CO}} = 1$)	This work ($\nu_{\text{CO}} = 1$)	Expt. (Ref. 3) ($\nu_{\text{CO}} = 0$)	This work ($\nu_{\text{CO}} = 0$)
$K = 0$				
σ	0.0	0.0	0.0	0.0
B_e	0.108 591 6	0.107 647 47	0.108 731 59	0.107 783 77
D_e	$0.128\,85 \times 10^{-4}$	$0.130\,80 \times 10^{-4}$	$0.128\,34 \times 10^{-4}$	$0.129\,21 \times 10^{-4}$
H_e	-0.370×10^{-8}	-0.276×10^{-8}	-0.379×10^{-8}	-0.393×10^{-8}
L_e	-0.387×10^{-11}	-0.214×10^{-11}	-0.376×10^{-11}	-0.216×10^{-11}
$K = 1$				
σ	3.1864	3.2570	3.2161	3.2861
B_e	0.104 102 3	0.103 238 40	0.104 264 83	0.103 397 73
D_e	$0.122\,61 \times 10^{-4}$	$0.117\,69 \times 10^{-4}$	$0.123\,38 \times 10^{-4}$	$0.119\,47 \times 10^{-4}$
H_e	-0.064×10^{-8}	-0.5677×10^{-8}	-0.160×10^{-8}	-0.589×10^{-8}
L_e	-4.222×10^{-11}	-2.860×10^{-11}	-4.234×10^{-11}	-2.919×10^{-11}
B_f	0.111 515 6	0.110 617 59	0.116 139 7	0.110 720 19
D_f	$0.127\,51 \times 10^{-4}$	$0.124\,02 \times 10^{-4}$	0.1253×10^{-4}	$0.124\,18 \times 10^{-4}$
H_f	-0.107×10^{-8}	-0.435×10^{-8}	-0.1198×10^{-8}	-0.4536×10^{-8}
L_f	-1.69×10^{-11}	-9.012×10^{-11}	-1.780×10^{-11}	-8.668×10^{-11}
$K = 2$				
σ	10.1547	10.2657	10.2548	10.3638
B_e	0.103 600	0.102 807	0.103 737	0.102 923 41
D_e	0.0880×10^{-4}	0.1683×10^{-4}	0.0908×10^{-4}	0.1706×10^{-4}
H_e	-63.48×10^{-8}	-64.56×10^{-8}	-65.40×10^{-8}	-66.09×10^{-8}
L_e	201.9×10^{-11}	221.2×10^{-11}	210.5×10^{-11}	224.8×10^{-11}
B_f	0.103 918	0.102 970 5	0.104 036	0.103 086 87
D_f	0.1206×10^{-4}	0.1212×10^{-4}	0.1206×10^{-4}	0.1179×10^{-4}
H_f	-1.203×10^{-8}	-1.243×10^{-8}	-1.245×10^{-8}	-1.553×10^{-8}
$K = 3$				
σ	20.8018	20.9815	21.0158	21.1870
B_e	0.111 198	0.107 342	0.106 039	0.105 567
D_e	2.284×10^{-4}	1.030×10^{-4}	1.049×10^{-4}	$1.014\,54 \times 10^{-4}$
H_e	170.1×10^{-8}	164.0×10^{-8}	75.7×10^{-8}	23.52×10^{-8}
L_e	-553.0×10^{-11}	-670.3×10^{-11}	-312.0×10^{-11}	-312.03×10^{-11}
B_f	0.101 627	0.101 248	0.101 050	0.100 258
D_f	-0.0421×10^{-4}	-0.3397×10^{-4}	-0.0744×10^{-4}	-0.0624×10^{-4}
H_f	-13.82×10^{-8}	-28.95×10^{-8}	-14.89×10^{-8}	-28.06×10^{-8}

to three quanta of bending excitation, mixed with one quantum of stretching.

C. Comparison with experiments

In 1998, McKellar and Chan³ measured the infrared spectra of the Ne–CO complex a tunable diode laser source to probe a low pressure (1.4 Torr) CO + Ne mixture in a long-path (160 m) low-temperature (47 K) absorption cell. They reported the $K = 2 \leftarrow 1$, $K = 1 \leftarrow 2$, $K = 3 \leftarrow 2$, $K = 2 \leftarrow 3$ subbands and involving the first excited bending state transitions of $(\nu_2, K) = (1,1) \leftarrow (1,0)$, $(1,0) \leftarrow (1,1)$, $(0,0) \leftarrow (1,0)$ subbands. In 1993, Randall,⁵ recorded infrared spectra of the Ne–CO complex. They observed the $\Sigma \leftarrow \Sigma$ subband and $\Sigma \leftarrow \Sigma^{\text{excited}}$ subband. We compare our *ab initio* values with the experimental results listed in Tables II–VI. It can be seen that the theoretical results are in good agreement with the experimental data. For the Table V of the Ref. 3, the author labeled the second observed with $(1,1) \leftarrow (0,1)$ but the results are the $(1,0) \leftarrow (1,1)$ subband and in the 3.2.4 section of the paper they described that the

subband is describe, so we think it is a printing error in the Table V. In Tables VII and VIII we also compared our results with the Robert's¹³ results, it obvious that our results are better than the Robert's.

In their analysis of the experimental spectrum of the Ne–CO, McKellar and Chan³ have used a quasirigid rotor formula for the rotational energy levels of this complex,

$$E_{\text{total}} = \sigma + BY - DY^2 + HY^3 + LY^4, \quad (21)$$

where σ is the level origin relative to the van der Waals ground state. In Tables IX and X we compare the experimental and theoretical spectroscopic constants of the van der Waals of Ne–CO complex. The fitting includes the calculated levels up to $J = 10$. The theoretical σ and B parameters agree with their experimental counterparts. There is a slight overestimation of the experimental results. In spite of the fairly large errors surmised by the experimental, on the higher order potential parameters, we clearly see that our calculated values are always of the same order of magnitude as that of experimental results and suggest a very similar set of spectroscopic parameters.

TABLE X. Spectroscopic constants (in cm^{-1}) of the van der Waals first excited intermolecular vibrational state of $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ complex.

	Expt. (Ref. 3) ($\nu_{\text{CO}} = 1$)	This work ($\nu_{\text{CO}} = 1$)	Expt. (Ref. 3) ($\nu_{\text{CO}} = 0$)	This work ($\nu_{\text{CO}} = 0$)
$K = 0$				
σ	8.4904	8.4246	8.858 05	8.810 66
B_e	0.105 606 1	0.104 894	0.105 612	0.104 907
D_e	$0.197\,32 \times 10^{-4}$	0.1800×10^{-4}	0.1953×10^{-4}	$0.188\,81 \times 10^{-4}$
H_e	1.860×10^{-8}	1.842×10^{-8}	1.78×10^{-8}	1.999×10^{-8}
L_e	-4.26×10^{-11}	-26.1×10^{-11}	-4.26×10^{-11}	-8.28×10^{-11}
$K = 1$				
σ	15.0194	14.9929	15.1457	15.122 26
B_f	0.107 782	0.107 013	0.107 707	0.106 904
D_f	0.1771×10^{-4}	0.1856×10^{-4}	0.1846×10^{-4}	0.1880×10^{-4}
H_f	-3.01×10^{-8}	-2.89×10^{-8}	-2.83×10^{-8}	-2.92×10^{-8}

IV. CONCLUSIONS

We have constructed a new high quality three-dimensional potential energy surface for the Ne–CO van der Waals complex using the CCSD(T) method and avqz/avqz+33221 basis set. The *ab initio* calculation is performed in a total of 1365 configurations with supermolecule method. The counterpoise procedure of Boys and Bernardi is used to correct for BSSE. The corrected *ab initio* single point interaction energies then are fitted to an analytic function. Using the five two-dimensional potentials, the three-dimensional potential is constructed by the interpolating along $(r - r_e)$ using a fourth-order polynomial. There is a single global minimum located in a nearly T-shaped geometry. The global minimum energy is -49.4090 cm^{-1} at $R_e = 6.40a_0$ and $\theta_e = 82.5^\circ$. The linear Ne–C–O geometry is lower in energy (-43.2824 cm^{-1} at $R = 7.00a_0$) than the linear Ne–O–C geometry (-31.2998 cm^{-1} at $R = 8.10a_0$). The potential is rather flat, making possible large amplitude motions.

Using the three-dimensional potential energy surface, we have calculated bound rovibrational energy levels up to $J = 10$ including the Coriolis coupling terms. Compared with the experimental transition frequencies, the theoretical results are in good agreement with the experimental results.

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