An *ab initio* study of the Ne–CO complex

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A new *ab initio* potential energy surface of the Ne–CO complex is developed using single and double excitation coupled-cluster theory with noniterative treatment of triple excitations [CCSD(T)]. The potential has a minimum value of -49.396 cm^{-1} at $R_e = 6.40a_0$ with approximately T-shaped geometry ($\theta_e = 82.5°$). Bound state energies are calculated up to $J = 12$. The theoretically predicted transition frequencies and spectroscopic constants are in good agreement with the available experimental results.

Keywords: Ne–CO complex, potential energy surface, bound state, spectra

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1. Introduction

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

All of the Rg–CO complexes have been studied experimentally.[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 ^{3}He and ^{4}He. Chan and McKellar[2] used 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[3] 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. The first experimental study of infrared spectrum for the Ar–CO complex was reported by McKellar *et al.*[5] in 1992. They assigned six *b*-type transitions (with $\Delta K = \pm 1$) for K values up to 3 in the CO fundamental band. In 1996, Xu *et al.*[6] extended this work to K values up to 6. McKellar[7] observed the infrared spectra of Kr–CO and Xe–CO complexes 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 McKellar[8] also recorded the infrared spectra of the both complexes. In 2001, millimeter-wave spectroscopy of the Kr–CO and Xe–CO complexes was reported by Walker and McKellar[9] using a coaxial jet spectrometer.

On the theoretical[10−14] side, much attention has been paid to Rg–CO complexes. For instance, in 2005, Peterson and McBane[10] constructed the three-dimensional potential energy surface (PES) of the He–CO complex. They employed the CCSD(T) method and extrapolated the individual counterpoise-corrected interaction energy to the 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 had rms error and maximum errors of just 0.03 and 0.04 cm^{-1}, respectively. McBane and Cybulski[11] reported the two-dimensional PES of the Ne–CO complex in 1999. The theoretical results were in good agreement with the experimental data. In 2002, Pedersen and Koch[12] 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[13] and Xe–CO complex.[14] Bound state energies were calculated up to $J = 12$. The predicted transition frequencies and spectroscopic constants were in good agreement with the experimental results.

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2. Potential energy surface

2.1. *Ab initio* calculation

Jacobi coordinates are used throughout the present work. In these coordinates, $r_{\rm CO}$ is the CO bond length, R refers to the distance between the Ne atom and the centre of mass of CO molecule, and θ is the angle between R and $r_{\rm CO}$ with $r_{\rm CO}$ = 180° referring to the Ne–C–O linear configuration. The interaction potential energy surface of the Ne–CO complex is calculated at the coupled cluster single and double levels of theory with a perturbative treatment of the connected triple excitations, CCSD(T).[15−17] Dunning's augmented correlation-consistent polarized valence quadrupole-ζ (aug-cc-pVQZ) basis set is chosen for Ne, O and C atoms. Midbond functions (3s3p2d2f1g) (for 3s and 3p, α = 0.9, 0.3 and 0.1; for 2d and 2f, α = 0.6 and 0.2; for g, α = 0.3) are used to eliminate the need for higher angular momentum functions in the atom-centred basis set. We denote this basis set by avqz +33221.

The CCSD(T) calculations are performed using the MOLPRO 2006 package.[1)] The supermolecule approach is employed to obtain the intermolecular potential energy for each configuration. Calculations are performed over 18 values of the intermolecular separation (R = 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10, 11, 12, 13, 14, 15, 16 and 17a_0), and over 13 angles (θ = 0, 20, 40, 60, 80, 90, 105, 115, 125, 135, 150, 165 and 180 degrees), resulting in a PES consisting of a total of 234 configurations. We also use the counterpoise procedure of Boys and Bernardi to correct for basis set superposition error (BSSE).[18] In all calculations the CO bond length is fixed at the experimentally determined value of 2.132a_0.

2.2. Fitting procedure

The PES is constructed by fitting the *ab inito* interaction energies in grid-points to the analytic function $V(R,\theta)$, originally suggested by Bukowski *et al.*[19] which has been used in several similar systems.[2,20] The function is the sum of two terms, the short range term $V_{\rm sh}$ and the asymptotic term $V_{\rm as}$:

$$V(R,\theta) = V_{\rm sh}(R,\theta) + V_{\rm as}(R,\theta), \tag{1}$$

where

$$V_{\rm sh}(R,\theta) = G(R,\theta)\mathrm{e}^{B(\theta)+D(\theta)R}, \tag{2}$$

and

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

The sum over l starts from 0 when n is even, otherwise it begins with l = 1. $D(\theta)$, $B(\theta)$, and $G(R,\theta)$ are all expansions in Legendre polynomials ($P_l^0(\cos\theta)$):

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

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

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

Here, b_l, d_l, g_{kl}, and C_{nl} are adjustable parameters. The $f_n(x)$ is the Tang–Toennies damping function,

$$f_n(x) = 1 - \mathrm{e}^x \sum_{k=0}^{n} \frac{x^k}{k!}. \tag{7}$$

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.[21] In the first step, we fit the *ab initio* values with $R \geq 9.5a_0$ using only the n = 6 and 7 terms of the long-range function $V_{\rm as}$, with the damping function set to one. In the second step, we fix the long-range coefficients for n = 6 and determine all other parameters including the n = 7, 8, 9 long range coefficients. The global rms error of the fitting was found to be 0.025 cm^{-1} and the maximum absolute error was 0.095 cm^{-1} for all grid-points excluding grid-points with $V > 500$ cm^{-1}. In the vicinity of the potential well, $6.5a_0 \leq R \leq 9.5a_0$ and $V < 0$, the absolute error was less than 0.02 cm^{-1} and the relative error was less than 0.04%. In the long range, the relative error was within 0.8%. Table 1 lists all the fitting coefficients.

[1)] MOLPRO is a package of *ab initio* programs written by Werner H J and Knowles P J, with contributions from Amos R D, Berning A, Cooper D L *et al.*

Table 1. Coefficients of the analytical PES fitted to the avqz+33221 value of interaction energies.

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
b	15.5771	1.31540	0.704194	−0.227336	−0.0395289	0.0329861
d	−2.07517	−0.164850	−0.0536975	0.0352392	0.0137142	−0.00174538
g_0	5.28867	0.979375	−0.457977	−0.100695	0.481392	−0.487237
g_1	−1.11283	−0.380193	0.0135643	0.597467	−0.144237	0.243244
g_2	0.964344	−1.24843	1.28841	−0.772897	0.208409	−0.0858265
g_3	−0.0957915	0.133676	−0.134154	0.0750523	−0.0197970	0.00628318
$C_{60}=-4.636277\times10^6$, $C_{62}=-5.448036\times10^5$, $C_{71}=1.709642\times10^7$, $C_{73}=3.149917\times10^6$,						
$C_{80}=-1.761611\times10^8$, $C_{82}=-1.752012\times10^8$, $C_{84}=-8.724042\times10^6$, $C_{91}=3.510852\times10^8$,						
$C_{93}=3.510852\times10^7$, $C_{95}=6.358690\times10^6$,						

2.3. Features of the surface

A contour plot of the PES is shown in Fig. 1. There is obviously a single global minimum located in a near T-shaped geometry. The global minimum energy is −49.396 cm^{-1} at $R_e = 6.40a_0$ and $\theta_e = 82.50°$. The linear Ne–O–C geometry is lower in energy (−43.196 cm^{-1} at $R = 7.00a_0$) than the linear Ne–C–O geometry (−31.267 cm^{-1} at $R = 8.10a_0$). The potential surface is seen to be rather flat, making possible large amplitude motions.

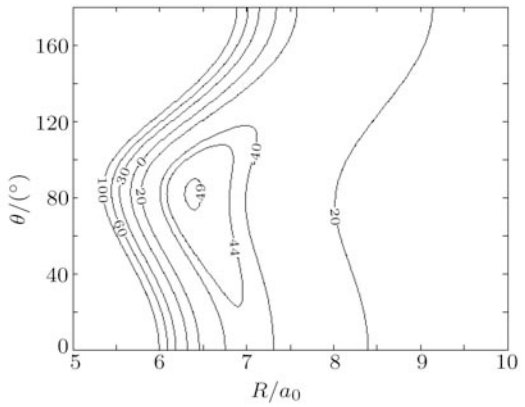


Fig. 1. Contour plot of the avqz+33221 potential energy surface for the Ne–CO complex (in cm^{-1}).

3. Rovibrational energy levels calculation

3.1. Computational details

The rovibrational energy levels and wave functions are calculated with CO frozen at its equilibrium distance. This is considered to be a good approximation because the vibrational frequency of Ne and CO is about 10 cm^{-1}, which is at least two orders of magnitude lower than the CO ground state vibrational frequency of 2143 cm^{-1}. This approximation has been widely used for the RG–CO[11,13,14] complexes, such as He–CO, Ar–CO, Kr–CO and Xe–CO, and the results are in good agreement with the experimental values. For the Ne–CO complex, the theoretically predicted results are also reliable (see below). The Hamiltonian can then be expressed as[22]

$$H = -\frac{\hbar^2}{2mR}\frac{\partial^2}{\partial R^2}R + \frac{\hbar^2}{2mR^2}(\hat{J}-\hat{j})^2 + b_{\rm CO}\hat{j}^2 + V(R,\theta) \tag{8}$$

with

$$(\hat{J}-\hat{j})^2 = \hat{J}^2 + \hat{j}^2 - 2\hat{j}_Z\hat{J}_Z - \hat{j}_+\hat{J}_- - \hat{j}_-\hat{J}_+, \tag{9}$$

where $\hat{J}$ denotes the total angular momentum operator of the Ne–CO complex, $\hat{j}$ the angular momentum operator of rigid CO molecule and $b_{\rm CO}$ 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 $\hat{j}_x \pm {\rm i}\,\hat{j}_y$ and $\hat{J}_\pm$ for $\hat{J}_x \pm {\rm i}\,\hat{J}_y$.

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

$$H\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta) = E_i^{Jp}\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta). \tag{10}$$

The eigen-solutions are labeled by good quantum numbers: J for the total angular momentum of the Ne–CO complex, M for the magnetic quantum number, $p = \pm1$ for the total parity of the wave function. 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, firstly, the potential $V(R,\theta)$ is expanded into Legendre polynomials as

$$V(R,\theta) = \sum_{\lambda=0}^{\lambda_{\max}} V_\lambda(R)P_\lambda^0(\cos\theta). \tag{11}$$

Then, the wave functions are expanded into a basis set

$$\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta)=\frac{1}{R}\left(\frac{2J+1}{4\pi}\right)^{1/2}\sum_{q=0}^{q_{\max}}\sum_{j=0}^{j_{\max}}\sum_{k=0\,\mathrm{or}\,1}^{\min(j,J)}c_{q,jk}^{Jpi}\chi_q(R)\Phi_{jk}^{JMp}(\theta,\varphi,\alpha,\beta), \tag{12}$$

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

$$\Phi_{jk}^{JMp}(\theta,\varphi,\alpha,\beta)=N_k[D_{MK}^{J^*}(\alpha,\beta,0)Y_{jk}(\theta,\varphi)+p(-1)^J D_{M-K}^{J^*}(\alpha,\beta,0)Y_{j-k}(\theta,\varphi)]. \tag{13}$$

Here, $D_{MK}^{J^*}$ is an element of a Wigner rotation matrix, Y_{jk} a spherical harmonic. The normalization factor N_k is $1/2$ for $k=0$ and $1/\sqrt{2}$ for others. 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. In this work, the radial basis functions have been determined as numerical eigen-solutions to the vibrational Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}+V(R,82.5^\circ)\right]\chi_q(R)=E_q\chi_q(R), \tag{14}$$

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

$$\begin{aligned}H_{qjk,q'j'k'}=&\delta_{qq'}\delta_{jj'}\delta_{kk'}\left[E_q+b_{\mathrm{CO}}j(j+1)\right]+\left\langle\chi_q\left|\frac{\hbar^2}{2mR^2}\right|\chi_{q'}\right\rangle\left\langle\Phi_{jk}^{JMp}\left|(\hat{J}-\hat{j})^2\right|\Phi_{j'k'}^{JMp}\right\rangle\\&+\sum_\lambda\left\langle\chi_q\left|V_\lambda(R)-V_\lambda(R,82.5^\circ)\right|\chi_{q'}\right\rangle\left\langle\Phi_{jk}^{JMp}\left|P_\lambda^0(\cos\theta)\right|\Phi_{j'k'}^{JMp}\right\rangle.\end{aligned} \tag{15}$$

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.[23] When the discrete variable representation (DVR) method is used to solve the Eq. (14) the integral over R can be simply given by[23]

$$\langle\chi_q\left|g(R)\right|\chi_{q'}\rangle\doteq\sum_{i=1}^{N}\chi_q(R_i)g(R_i)\chi_{q'}(R_i), \tag{16}$$

where R_i is the ith 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 the solution of the corresponding secular equation.

3.2. Theoretical results

A self-written Fortran code[22] is used to calculate the rovibrational energy levels and wave functions of the Ne–CO complex. After careful testing, we expand the potential in Legendre polynomials up to $\lambda_{\max}=13$. The basis set parameters $j_{\max}$ and $q_{\max}$ are 40 and 60, respectively. The rotational constant b_{CO} of CO is 1.92253 cm^{-1} from the NIST Standard Reference Database.[24] The numerical integration over R was performed with 500 equidistant grids ranging from 5.0 to $17a_0$. We calculated the bound state energies for total angular momentum from $J=0$ to 12. We chose the $J_{\max}=12$ because then the theoretical results not only can completely compare with the experiment transition results, but also can give enough bound state energies to calculate the spectroscopic constants.

The wave functions of the first four $J=0$ vibrational levels are shown in Fig. 2 (a)–(d). The ground vibrational energy is $E_0=-31.4189$ cm^{-1}, which corresponds to a zero-point energy of 17.977 cm^{-1}. It can be seen that the contours of this state are mainly localized on the near T-shaped geometry. The first excited vibrational level at -22.8886 cm^{-1} corresponds basically to a bending excitation observed from the node structure. We thus deduce the bending ground frequency 8.530 cm^{-1}. The second excited level at -17.8581 cm^{-1} 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 -10.9576 cm^{-1} can be assigned to three quanta of bending excitation, mixed with one quantum of stretching.

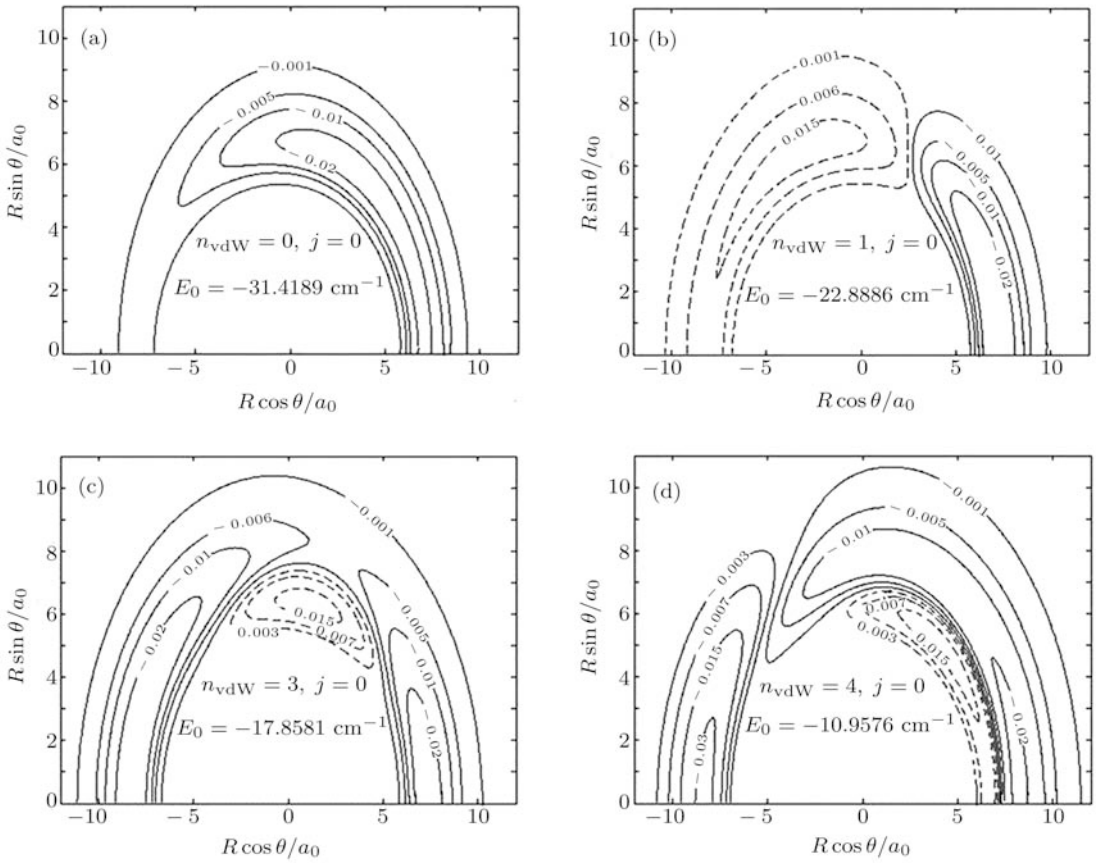


Fig. 2. Contours of the wave functions for the first four vibrational levels ($J = 0$) of Ne–CO complex.

3.3. Comparison with experiments

In 1997, Walker and McKellar[2] measured the microwave spectra of the Ne–CO complex using a pulsed jet, cavity microwave Fourier transform spectrometer. They reported the a-type R-branches transition with $\Delta J = +1$, $\Delta K_{\rm a} = 0$, and $\Delta K_{\rm c} = +1$. In Table 2, we present a comparison of our *ab initio* values of the ^{20}Ne–^{12}C–^{16}O complex with experimental results and the previous values. It can be seen that the our theoretical results are smaller than the experimental data in general and the errors range from 0.002 cm^{-1} to 0.007 cm^{-1}, which is of the same order of magnitude as that for the SAPT potential surface and better than that for the S2

Table 2. Observed and calculated rotational transitions of the ^{20}Ne–^{12}C^{16}O complex in its ground vibrational state $n_{\rm vdW} = 0$ (in cm^{-1}) and compared with the experimental results and the previous values. The Δ is the difference (Expt.–Calc.).

transition	Expt[2].	Calc. SAPT[10]	Δ	Calc. S2[10]	Δ	Calc. this work	Δ
1_{01}—0_{00}	0.21741	0.218	−0.001	0.213	0.004	0.21565	0.00176
2_{02}—1_{01}	0.43451	0.436	−0.001	0.427	0.007	0.43089	0.00363
2_{12}—1_{11}	0.41656	0.420	−0.003	0.410	0.007	0.41334	0.00331
2_{11}—1_{10}	0.44603	0.450	−0.004	0.440	0.006	0.44257	0.00346
3_{03}—2_{02}	0.65098	0.652	−0.002	0.639	0.012	0.64572	0.00528
3_{13}—2_{12}	0.62425	0.629	−0.005	0.615	0.013	0.61949	0.00477
3_{12}—2_{11}	0.66830	0.675	−0.007	0.659	0.009	0.66331	0.00501
4_{04}—3_{03}	0.86652	0.869	−0.002	0.851	0.016	0.85949	0.00704
4_{14}—3_{13}	0.83096	0.839	−0.008	0.817	0.014	0.82463	0.00635

Table 3. Observed and calculated rotational transitions of five isotopes Ne–CO complex in its ground vibrational state $n_{\rm vdW} = 0$ (in $\rm cm^{-1}$). For each transition the first line is the Calc., the second line is difference the (Expt.[2]–Calc.).

transition	^{21}Ne–^{12}C^{16}O	^{22}Ne–^{12}C^{16}O	^{20}Ne–^{13}C^{16}O	^{22}Ne–^{13}C^{16}O	^{20}Ne–^{13}C^{18}O
1_{01}—0_{00}	0.21001	0.20488	0.21362	0.20279	0.20832
	0.00171	0.00167	−0.00001	−0.00005	0.00122
2_{02}—1_{01}	0.41972	0.40948	0.42694	0.40531	0.41635
	0.00342	0.00333	−0.00003	−0.00005	0.00244
3_{03}—2_{02}	0.62885	0.61352	0.63966	0.60731	0.62383
	0.00513	0.00500	−0.00008	−0.00010	0.00365
4_{04}—3_{03}	0.83708	0.81673	0.85149	0.80850	0.83045
	...	0.00667	−0.00015	−0.00018	0.00483

surface. In Table 3, we list a comparison of the *ab initio* values with the experimental results of five other isotopes of the Ne–CO complex. The relative error ranges from 0.01% to 0.8%.

In their analysis of the experimental spectrum of the Ne–CO, the McKellar Group[1] have used a quasi-rigid rotor formula for the rotational energy levels of this complex

$$E_{\rm total} = \sigma + BY - DY^2 + HY^3 + LY^4, \qquad (17)$$

where $Y = J(J+1)$, σ is the level origin relative to the van der Waals ground state. Each stack of levels has an associated origin denoted by σ and a set of rotational parameters, B_n, D_n, etc., where $n(=\,\rm e\,or\,f)$ is a parity label. In Table 4 we compare experimental and theoretical spectroscopic constants of the van der Waals ground state of ^{20}Ne–^{12}C^{16}O complex. The fitting includes the calculated levels up to $J = 12$. The rms is $1.04 \times 10^{-8}\rm cm^{-1}$ for $K = 0$, $4.12 \times 10^{-7}\rm cm^{-1}$ for $K = 1$, $2.37 \times 10^{-7}\rm cm^{-1}$ for $K = 2$ and $5.82 \times 10^{-7}\rm cm^{-1}$ for $K = 3$. The theoretical σ and B parameters agree very well with their experimental counterparts. There is a slight overestimation of 0.26% for the stack origins σ and less than 0.9% underestimation of the B rotational constant. In spite of the fairly large errors surmised from the experiment, on the higher order potential parameters, we clearly see that our calculated values are always of the same order of magnitude as them and suggest a very similar set of spectroscopic parameters. We also calculate the molecular parameters for ^{20}Ne–^{12}C^{16}O in its fist excited intermolecular vibrational state and compared them with the experimental values list in Table 5. The fitting rms error is 3.245×10^{-8} $\rm cm^{-1}$, 8.13×10^{-7} $\rm cm^{-1}$, 1.357×10^{-7} $\rm cm^{-1}$ and 5.231×10^{-6} $\rm cm^{-1}$ for the $K = 0, 1, 2, 3$ of the $n_{\rm Vdw} = 1$ rovibrational levels, respectively.

Table 4. Spectroscopic constants (in $\rm cm^{-1}$) of the van der Waals ground state of ^{20}Ne–^{12}C^{16}O complex.

		Expt.[1]	this work
$K = 0$:	σ	0.0	0.0
	B_e	0.10873159	0.10783633
	D_e	0.12834×10^{-4}	0.12344×10^{-4}
	H_e	-0.379×10^{-8}	-0.1799×10^{-8}
	L_e	-0.376×10^{-11}	-0.8305×10^{-11}
$K = 1$:	σ	3.2161	3.2241
	B_e	0.10426483	0.10343939
	D_e	0.12338×10^{-4}	0.10672×10^{-4}
	H_e	-0.160×10^{-8}	-0.2042×10^{-8}
	L_e	-4.234×10^{-11}	-7.117×10^{-11}
	B_f	0.11161397	0.11075109
	D_f	0.12653×10^{-4}	0.112166×10^{-4}
	H_f	-0.1198×10^{-8}	-0.2648×10^{-8}
	L_f	-1.780×10^{-11}	-1.244×10^{-11}
$K = 2$:	σ	10.2548	10.281341
	B_e	0.103737	0.10320208
	D_e	0.0908×10^{-4}	0.08950×10^{-4}
	H_e	-65.40×10^{-8}	-35.76×10^{-8}
	L_e	210.5×10^{-11}	253.8×10^{-11}
	B_f	0.104036	0.10318045
	D_f	0.1206×10^{-4}	0.1159×10^{-4}
	H_f	-1.245×10^{-8}	-3.24155×10^{-8}
$K = 3$:	σ	21.0158	21.070784
	B_e	0.106039	0.105321702
	D_e	1.049×10^{-4}	1.00558×10^{-4}
	H_e	75.7×10^{-8}	15.47×10^{-8}
	L_e	-312.0×10^{-11}	$-653.4055 \times 10^{-11}$
	B_f	0.101050	0.1003484
	D_f	-0.0744×10^{-4}	-0.0663×10^{-4}
	H_f	-14.89×10^{-8}	-83.307×10^{-8}

Table 5. Spectroscopic constants (in cm^{-1}) of the van der Waals first excited intermolecular vibrational state of the ^{20}Ne–$^{12}C^{16}O$ complex.

		Expt[1]	this work
$K = 0$:	σ	8.85805	8.8002769
	B_e	0.105612	0.10489961
	D_e	0.1953×10^{-4}	$0.17473919 \times 10^{-4}$
	H_e	1.78×10^{-8}	3.1462×10^{-8}
	L_e	-4.26×10^{-11}	-8.53×10^{-11}
$K = 1$:	σ	15.1457	15.12508
	B_f	0.107707	0.1064293
	D_f	0.1846×10^{-4}	0.1369×10^{-4}
	H_f	-2.83×10^{-8}	-5.22×10^{-8}

Table 6. Lists the temperature dependence of the interaction second virial coefficient of the Ne–CO complex (in units of $ml \cdot mol^{-1}$), and compared with the experimental results and the previous values.

T/K	Expt.	SAPT	S2	this work
123.15	-14.7 ± 3.0	-17.26	-14.48	-14.17
148.15	-5.6 ± 3.0	-7.50	-5.28	-5.03
173.15	-0.42 ± 3.0	-0.96	0.90	1.09
223.15	7.83 ± 2.0	7.15	8.57	8.69
273.15	12.23 ± 2.0	11.88	13.04	13.11
296.15	14.1 ± 1.5	13.43	14.35	14.56
353.15	17.2 ± 2.0	16.24	17.03	17.18
463.15	20.6 ± 3.0	19.34	19.97	20.04

We also calculated the second virial coefficients of the Ne–CO complex. The second virial coefficients are sensitive to the depth and volume of the attractive well at low temperatures, and to the volume of the repulsive core at high temperatures. They are spherically averaged quantities and are not very sensitive to anisotropy. Table 6 shows the comparison of *ab initio* values with experimental results and previous values.[10] It was found that our results are better than the results for the SAPT potential. Compared with the S2 potential, our results are better at high temperatures.

4. Conclusion

We have developed a new high quality potential energy surface for the Ne–CO van der Waals complex using the CCSD(T) method and avqz+33221 basis set. The *ab initio* calculation was performed in a total of 234 configurations with the supermolecule method. The counterpoise procedure of Boys and Bernardi is used to correct for basis set superposition error (BSSE). The corrected *ab inito* single point interaction energies then are fitted to an analytic function. It was found that there is a single global minimum located in a near T-shaped geometry. The global minimum energy is -49.396 cm^{-1} at $R_e = 6.4a_0$ and $\theta_e = 82.5°$.

Using the fitted potential energy surface, we have calculated bound rovibrational energy levels up to $J = 12$, including the Coriolis coupling terms. Compared with the experimental transition frequencies, the relative error is less then 0.8%. The theoretical spectroscopic constants in the van der Waals ground vibrational state and first excited intermolecular vibrational state are also in good agreement with the experimental results. We also calculated the second virial coefficients of the Ne–CO complex, the results are in agreement with the experimental results.

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