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An exchange-Coulomb model potential energy surface for the Ne–CO interaction. I. Calculation of Ne–CO van der Waals spectra

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Exchange-Coulomb model potential energy surfaces have been developed for the Ne–CO interaction. The initial model is a three-dimensional potential energy surface based upon computed Heitler–London interaction energies and literature results for the long-range induction and dispersion energies, all as functions of interspecies distance, the orientation of CO relative to the interspecies axis, and the bond length of the CO molecule. Both a rigid-rotor model potential energy surface, obtained by setting the CO bond length equal to its experimental spectroscopic equilibrium value, and a vibrationally averaged model potential energy surface, obtained by averaging the stretching dependence over the ground vibrational motion of the CO molecule, have been constructed from the full data set. Adjustable parameters in each model potential energy surface have been determined through fitting a selected subset of pure rotational transition frequencies calculated for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{12}\mathrm{O}$ isotopolog to precisely known experimental values. Both potential energy surfaces provide calculated results for a wide range of available experimental microwave, millimeter-wave, and midinfrared Ne–CO transition frequencies that are generally far superior to those obtained using the best current literature potential energy surfaces. The vibrationally averaged CO ground state potential energy surface, employed together with a potential energy surface obtained from it by replacing the ground vibrational state average of the CO stretching dependence of the potential energy surface by an average over the first excited CO vibrational state, has been found to be particularly useful for computing and/or interpreting mid-IR transition frequencies in the Ne–CO dimer. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3157169]

I. INTRODUCTION

Following its initial development and introduction as an efficient and accurate means of modeling closed shell atom-atom interaction energies (see Refs. 1–6 and references therein), the exchange-Coulomb (XC) model has been extended to provide accurate representations of the interaction energies between rare-gas (Rg) (He, Ne, Ar, Kr) atoms and homonuclear (H_2, N_2) diatomic molecules[7–13] and between He and CO.[14] The current XC model for the dimer interaction energy employs Heitler–London first-order interaction energies to describe the predominantly repulsive short-range behavior and individually damped and overall-corrected dispersion energies to describe the predominantly attractive long-range behavior (see Ref. 15 and, for example, Ref. 12 for a more detailed description). The model contains *ad hoc* adjustable parameters through a function multiplying the Heitler–London energy term; the input dispersion energy coefficients are also treated as additional adjustable parameters (but only within their estimated uncertainties). Optimal values for the full set of adjustable parameters can be determined by fitting the potential to highly accurate experimental microwave (MW) and/or infrared (IR) spectral transitions of the van der Waals dimer, together with the temperature dependence of a bulk property, such as the second virial coefficient for a pure gas or the interaction second virial coefficient for a binary gas mixture.

Although the adjustable parameters for the final, XC(fit), potential energy surfaces (PESs) constructed for the $H_2-\mathrm{Ar},\mathrm{Kr}$ interactions[7,8] were determined primarily on the basis of fits to accurate spectroscopic data, these potential surfaces have also been shown to give excellent agreement with experimental data for phenomena that were not utilized in the fitting procedure. For the $H_2-\mathrm{Ar}$ interaction, calculated and measured inelastic differential scattering data, hyperfine transition frequencies,[7] and, to a more limited extent, gas phase nuclear magnetic relaxation times[16] have been compared, while for the $H_2-\mathrm{Kr}$ interaction, comparison has been made between calculated and measured temperature dependences of the interaction second virial and binary diffusion coefficients.[8] In all cases, the XC(fit) PESs have fared well.

MW spectroscopic data and the temperature dependences of the interaction second virial coefficients have been employed to determine the adjustable parameters in the final XC PESs for the $N_2-\mathrm{Ne},\mathrm{Ar},\mathrm{Kr}$ interactions:[10–12] These PESs have been found to provide excellent overall agreement with bulk transport and relaxation data in all three cases and, additionally, with extant experimental data for the IR spectrum of the $N_2-\mathrm{Ar}$ complex. As no MW data are available for the $N_2-\mathrm{He}$ van der Waals complex, the tem-

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perature dependences of interaction second virial coefficient data and of accurate diffusion data were utilized[13] to determine a N_2-He XC(fit) PES: This PES has been found to be of similar quality to the XC(fit) PESs for the N_2-Ne, Ar, Kr interactions.

The only case for which an XC(fit) PES has been determined for the interaction between a closed-shell atom and a closed-shell heteronuclear diatomic molecule is that of He with CO.[14] The He–CO van der Waals complex, unlike the $He-N_2$ complex, possesses a well-defined and relatively simple IR spectrum at low temperatures, so that the van der Waals dimer spectrum could be employed, together with the temperature dependence of the interaction second virial coefficient, to determine appropriate values for the fitting parameters. The He–CO XC(fit) PES not only provides an excellent fit to the positions of the IR spectral lines of the He–CO dimer but also predicts the various transport properties of He–CO bulk gas mixtures better than other available high-quality PESs, such as the $V_{(3,3,3)}$ PES of Chuaqui *et al.*[17] and the symmetry-adapted perturbation theory (SAPT) PESs of Moszynski *et al.*[18] and Heijmen *et al.*[19] (see Refs. 20–22). It was found,[23] however, not to predict the experimental rovibrational energy levels of the $^4He-^{13}C^{16}O$ isotopolog as accurately as the $V_{(3,3,3)}$ PES of Ref. 17.

Given the accuracy with which PESs representing interactions between Rg atoms and H_2 and N_2 molecules[7–13] and between He and the CO molecule[14,20] can be constructed, as shown by the ability of such PESs to predict MW and IR spectra of $Rg-N_2$ and He–CO van der Waals dimers and bulk properties of $Rg-N_2$ and He–CO binary mixtures, it is worthwhile to apply the XC model to the description of other Rg–CO interaction energies. The purpose of the present paper is to examine the simplest such Rg–CO interaction, namely, the Ne–CO interaction, as the Ne–CO van der Waals dimer has recently been the subject of a number of spectroscopic investigations, including MW,[24] millimeter-wave[25–27] (MMW), and midinfrared[28,29] (mid-IR) measurements. Special emphasis will be placed upon the use of the MW spectroscopic information for the predominant Ne–CO isotopolog to refine the potential parameters in the initial model PES and then upon the ability of the MW spectra for other Ne–CO isotopologs and of all Ne–CO MMW and IR spectra to establish the spectral reliability of the final XC(fit) PES.

Moszynski *et al.*[30] were the first to carry out a high-level *ab initio* quantum mechanical evaluation of the Ne–CO interaction energy as a function of the interspecies separation R and the angle θ lying between the interspecies axis and the CO bond axis. Their work was motivated in part by the existence of the mid-IR spectroscopic results of Ref. 28 and in part by the potentially interesting dynamics associated with a van der Waals dimer, such as Ne–CO, that is neither a semirigid molecule nor a complex in which the CO molecule is freely rotating. The SAPT method[31,32] was employed to calculate a two-dimensional (2D) PES for the Ne–CO interaction with the CO bond length fixed at the experimental equilibrium value[33] $r_e=2.132a_0$, and the PES was utilized for the calculation of the positions of the mid-IR spectral lines for comparison with the experimental results of Ref. 28. The resultant SAPT PES,[30] with a global minimum energy of $-53.4\ \text{cm}^{-1}$ for $R=6.34a_0$ and $\theta=92.2°$ ($\theta=0°$ corresponds to the collinear alignment Ne–C–O in the present study, cf. Refs. 30 and 34 in which the opposite convention is employed), gave rise to reasonable agreement between calculated and experimental transition frequencies. A slight scaling to allow for differences between the $Ne-CO(v_{CO}=0)$ and $Ne-CO(v_{CO}=1)$ interactions led to a significant improvement in the levels of agreement.

To improve the quality of the PES for short-range separations of Ne and CO, McBane and Cybulski[34] carried out supermolecule calculations at the coupled-cluster singles, doubles, and perturbative triples [CCSD(T)] level of theory. They obtained a PES, which they called the S2 PES, with a global minimum energy of $-48.54\ \text{cm}^{-1}$ for $R=6.397a_0$ and $\theta=80.15°$. While the S2 PES does not describe the ground state geometry as well as the SAPT PES,[34] it does provide a better representation of the short-range repulsive interaction according to comparisons made with experimental results that depend upon close approaches between Ne and CO, such as state-to-state integral cross section data[35] and state-to-state differential cross sections[36] from molecular beam scattering experiments. Because the S2 PES provides an improved description of the repulsive wall, it has also been employed for simulations of rotational relaxation rates.[37]

Finally, for completeness, it should be mentioned that a lower-level supermolecule calculation of the Ne–CO interaction energy (at the MP4 level) has been carried out by Subramanian *et al.*[38] for a fixed CO separation $r=2.132a_0$, giving a global minimum energy of $-22.6\ \text{cm}^{-1}$ at $R=6.76a_0$ and $\theta=60°$.

Section II describes the input data employed to construct the XC potential energy model, outlines the construction of a three-dimensional (3D) XC0 Ne–CO PES, and the determination both of a rigid-rotor 2D XC model PES corresponding to CO molecules with fixed CO separation r_e and of a vibrationally averaged 2D XC model PES applicable to interactions between Ne atoms and CO molecules in their ground vibrational ($v_{CO}=0$) state. An extension of the $Ne-CO(v_{CO}=0)$ PES to give a PES relevant to the interaction between Ne atoms and CO molecules in their first excited ($v_{CO}=1$) vibrational state is also described in this section. Section III focuses upon the angle dependence of representative features of the interaction, such as the position R_m and depth ϵ_m of the minimum in the interaction energy and the position σ at which the interaction energy vanishes. Comparisons are made between the values of these characteristic features for the XC PESs developed herein and other recently developed PESs, such as the *ab initio* SAPT PES plus a scaled SAPT PES obtained by Moszynski *et al.*[30] and the *ab initio* supermolecule CCSD(T) PES of McBane and Cybulski.[34] Section IV contains detailed comparisons for MW, MMW, and mid-IR spectroscopic transition frequencies calculated using the XC PESs and the *ab initio*/scaled SAPT PESs of Ref. 30 with the experimental results of Refs. 24–29 Finally, Sec. V presents a short summary of the XC PESs developed here plus conclusions drawn from the comparisons made in Secs. III and IV involving the present XC Ne–CO PESs, previously proposed Ne–CO PESs, and the various spectroscopic experimental results of Refs. 24–29.

II. THE NE–CO EXCHANGE-COULOMB MODEL POTENTIAL SURFACE

A convenient means for describing the dynamics of the van der Waals dimer formed from an atom and a diatomic molecule is to use Jacobi coordinates $\mathbf{r}=r\hat{\mathbf{r}}$, $\mathbf{R}=R\hat{\mathbf{R}}$, and $\theta=\cos^{-1}(\hat{\mathbf{r}}\cdot\hat{\mathbf{R}})$, in which $\hat{\mathbf{r}}$ is a unit vector directed along the axis of the diatomic molecule, r is the diatom bond length, $\hat{\mathbf{R}}$ is a unit vector defining the direction of the interspecies axis joining the centers of mass of the atom and the diatomic molecule, R is the interspecies separation (the distance between the centers of mass of the two species), and θ is the Jacobi angle between the interspecies and CO axes. Moreover, for those cases in which the diatom bond length r is not held fixed, in practice it is often replaced[7,8] by the dimensionless stretching coordinate $\xi\equiv(r-r_0)/r_0$ defined in terms of a fixed reference distance r_0. For a molecule in its ground vibrational state, for example, a reasonable choice for r_0 is the expectation value of r, which for CO has the value[39] $r_0\equiv r_0(\mathrm{CO})=2.139\,93a_0$.

A 2D PES with the CO bond distance set at a value characteristic of the CO molecule, such as r_0 or r_e, is appropriate for the calculation of line positions in the MW and MMW spectra of Ne–CO complexes formed with CO in its ground ($v_{\mathrm{CO}}=0$) vibrational state, of the energy and scattering angle dependence of molecular beam differential and integral cross sections, and of most bulk gas phenomena, such as the interaction second virial coefficient, binary diffusion and other mixture transport coefficients, of the rates of rotational relaxation, and of many other bulk gas relaxation phenomena. Obvious exceptions are the calculation of vibrational relaxation times[40–42] and IR vibrational transition frequencies.[7,8,43]

The variant of the XC model to be employed here is a diatom bond-length-dependent extension[7,8] of the 2D individually damped XC model, originally developed to describe closed-shell atom-atom interactions (see Refs. 1–6 and references therein) and successfully extended to Rg-diatom interactions.[9–15] The current XC model for the interaction energy is given as a sum of repulsive and attractive terms as

$$\begin{aligned}E_{\mathrm{int}}(R,\theta,\xi) &= F(R,\theta,\xi)E_{\mathrm{HL}}^{(1)}(R,\theta,\xi)+\Delta E_C(R,\theta,\xi)\\ &= F(R,\theta,\xi)E_{\mathrm{HL}}^{(1)}(R,\theta,\xi)\\ &\quad - G_{10}(R,\theta,\xi)\sum_{n=6}^{10} f_n(R,\theta,\xi)C_n(\theta,\xi)R^{-n}. \qquad (1)\end{aligned}$$

The mostly repulsive part of the potential energy is represented by the Heitler–London first-order interaction energy $E_{\mathrm{HL}}^{(1)}$, given by the sum of the first-order Coulomb and exchange energies for the atom-diatom complex, multiplied by an adjustable function F, with F normally determined through a fit to experimental data. The mostly attractive part, ΔE_C, of the PES models the Coulomb interaction energy past first order and is adequately represented by an individually damped, overall-corrected, dispersion-plus-induction energy series through R^{-10}. The individual damping functions[44] f_n that multiply the R^{-n} contributions model charge-overlap effects[44,45] that prevent these inverse-power terms from diverging as R decreases and are neglected in the usual multipolar expansion of ΔE_C. Finally, the overall corrector function G_{10} takes account of those effects[1–6] that are not represented in the model with $G_{10}=1$.

The long-range multipolar interaction energy coefficients $C_n(\theta,\xi)$ in Eq. (1) are represented by Legendre expansions having the form

$$C_n(\theta,\xi)=\sum_{\ell=0}^{n-4} C_n^{(\ell)}(\xi)P_\ell(\cos\theta), \qquad (2)$$

with $C_n^{(\ell)}\equiv 0$ when $n+\ell$ is odd. The coefficients $C_n^{(\ell)}(\xi)$ have both dispersion and induction contributions. The ξ dependence of these coefficients is represented by a cubic polynomial in ξ, given generically as

$$C_n^{(\ell)}(\xi)=\sum_{k=0}^{3}\left[C_{nk,\mathrm{disp}}^{(\ell)}+C_{nk,\mathrm{ind}}^{(\ell)}\right]\xi^k. \qquad (3)$$

A. Construction of a 3D XC model Ne–CO PES

Heitler–London interaction energies have been computed using the CADPAC implementation[46] of the Hayes–Stone perturbation theory program,[47] with monomer self-consistent field (SCF) wave functions ϕ_{Ne} and ϕ_{CO} calculated using CADPAC with basis sets constructed from Cartesian Gaussian primitives; the general approach used is that discussed earlier for interactions between H_2 or N_2 with fixed bond length and Rgs.[48] A SCF wave function for Ne has been obtained using the $14s7p$ basis set of Schmidt and Ruedenberg,[49] while the standard CADPAC ($8s6p3d$) basis sets for the C and O atoms were used (as was done previously[14] for He–CO) to compute the SCF wave functions for CO. The Heitler–London energies were obtained at 7 values of R ($4a_0\le R\le 10a_0$) and 15 values of θ ($0\le\theta\le 180$) for each of three CO bond lengths r ($2.0a_0$, $2.14a_0$, $2.30a_0$). The 315 computed energies (all in Hartree units, E_{h}) have been fitted to the form

$$E_{\mathrm{HL}}^{(1)}(R,\theta,\xi)=10^{-3}\exp\left[\alpha_0+R\sum_{i=1}^{3}\alpha_i z^{i-1}+\sum_{k=2}^{3}b_k\cos^k\theta\right]\sum_{\lambda=0}^{6}\sum_{p=0}^{5}\sum_{n=0}^{2}a_{\lambda p}^{(n)}\xi^n R^p P_\lambda(\cos\theta), \qquad (4)$$

in which $P_\lambda(\cos\theta)$ is a Legendre polynomial and z is defined as $z=(R-R_0)/(R+R_0)$, with $R_0=7.01a_0$. In the least-squares fit, the weight associated with each $E_{\mathrm{HL}}^{(1)}(R,\theta,\xi)$ datum is given by the reciprocal of its value. Values for the coefficients α_i, b_k, and $a_{\lambda p}^{(n)}$ have been provided in Table A.1 of the accompanying EPAPS document;[50] this set of values corresponds to a root-mean-square deviation (RMSD) of 0.57% from the *ab initio* data points.

The bond-stretching dependences of both the long-range dispersion and induction energy coefficients for $n=6$, 7, and 8, have been determined from the many-body perturbation theory (MBPT) results of Hettema *et al.*[51] for CO bond distances $r=2.00a_0$, $2.07a_0$, $2.14a_0$, $2.20a_0$, and $2.30a_0$. The expressions for the dispersion parts of $C_6^{(0)}(\xi)$ and $C_6^{(2)}(\xi)$ have been constrained to reproduce the dipole oscillator-strength-distribution results of Refs. 52 and 53. This has been accomplished, following previous work,[7,8] by employing the expectation values of ξ^n, $n=0,\ldots,3$, for CO in its ground vibronic state (specific values for these quantities can be found in Table A.1 of Ref. 50). The MBPT induction parts of $C_6^{(0)}(\xi)$ and $C_6^{(2)}(\xi)$ have been adjusted, following Ref. 14, by normalizing the bond-stretch dependence of the dipole moment of CO to the experimental value[54] $-0.048ea_0$ at $r=2.14a_0$ (the MBPT value[51] is $-0.186ea_0$). The stretching dependences of $C_{9,\mathrm{disp}}^{(1)}$ and $C_{9,\mathrm{disp}}^{(3)}$ have been estimated by assuming the form of the ξ dependence of $C_{7,\mathrm{disp}}^{(1)}$ obtained from the results of Ref. 51 but normalized to the values 2719.8 $E_\mathrm{h}a_0^{-9}$ and 1250.9 $E_\mathrm{h}a_0^{-9}$, respectively, obtained by Thakkar *et al.*[55] for $r=2.132a_0$. Similarly, $C_{10,\mathrm{disp}}^{(2)}(\xi)$ and $C_{10,\mathrm{disp}}^{(4)}(\xi)$ have been estimated from the ξ dependence of $C_{8,\mathrm{disp}}^{(2)}(\xi)$, in this case normalized to the values 23 036 $E_\mathrm{h}a_0^{-10}$ and 4037.3 $E_\mathrm{h}a_0^{-10}$, respectively, for $r=2.132a_0$ obtained in Ref. 55. Finally, $C_{10,\mathrm{disp}}^{(0)}(\xi)$ has been obtained, following Thakkar and Smith, Jr.,[56] by employing the ξ dependence of $[C_{8,\mathrm{disp}}^{(0)}(\xi)]^2/C_{6,\mathrm{disp}}^{(0)}\times(\xi)$ normalized to the value[55] 16 065 $E_\mathrm{h}a_0^{-10}$ for $r=2.132a_0$. It has, however, not been possible to make reasonable estimates of the stretching dependence either of $C_{9,\mathrm{disp}}^{(5)}\times(\xi)$ or of $C_{10,\mathrm{disp}}^{(6)}(\xi)$, as no values other than $C_{9,\mathrm{disp}}^{(5)}=-49.90$ $E_\mathrm{h}a_0^{-9}$ and $C_{10,\mathrm{disp}}^{(6)}=-204$ $E_\mathrm{h}a_0^{-10}$ for $r=2.132a_0$ are available.[55] The values of the coefficients $C_{nk,\mathrm{disp}}^{(l)}$ and $C_{nk,\mathrm{ind}}^{(l)}$ occurring in Eq. (3), $n=6-10$, used in constructing the 3D XC potential for Ne–CO can be found, respectively, in Tables A.2 and A.3 of Ref. 50. For $n\geq 9$ all induction energy coefficients have been omitted as no values are available in the literature for them. Note, however, that in general the induction components of the $C_n^{(l)}$ are much smaller than the analogous dispersion energy components.

The multipolar representation of the long-range interaction energy used for ΔE_C in Eq. (1) is based not only on the best available values of the $C_n(\theta,\xi)$ coefficients[51–53,55] which, in general, contain both dispersion and induction contributions, but also on a key feature of the XC model in terms of the corrector and damping functions, G_{10} and f_n, that appear in the second term of Eq. (1). These functions are defined, as in previous applications, by scaling the precisely known[3,5,44] analogous functions for the prototypical nonbonded H–H($a\ ^3\Sigma_u^+$) interaction via

$$\begin{aligned} f_n(R,\theta,\xi) &\equiv f_n(R,\theta) \\ &= [1-\exp\{-A_nSR - B_n(SR)^2 - D_n(SR)^3\}]^n, \end{aligned} \tag{5}$$

$$G_{10}(R,\theta,\xi) \equiv G_{10}(R,\theta) = 1 + 41.34e^{-0.8588SR}, \tag{6}$$

in which S is a system-dependent scaling factor. For $n=6$, 8, and 10, the coefficients A_n, B_n, and D_n are those determined for the H–H($a\ ^3\Sigma_u^+$) interaction, for which the scaling factor S is identically equal to unity, while for $n=7$ and 9, they have been generated by assuming, following Ref. 57, that $f_n=[f_{n-1}f_{n+1}]^{1/2}$; these coefficients can be found in Table A.4 of Ref. 50. Here, as has been done previously,[14] the induction energy damping functions are taken to be the same as for the dispersion energies for a given value of n.

As in previous work with the XC model, the scaling factor S utilized to map the functions derived for $\mathrm{H}_2(a\ ^3\Sigma_u^+)$ onto the range of the Ne–CO potential energy is defined as $S=R_m^{\mathrm{H}_2}/R_m(\theta)$, in which $R_m^{\mathrm{H}_2}=7.82a_0$ is the value for the equilibrium distance associated with the $\mathrm{H}_2(a\ ^3\Sigma_u^+)$ potential energy and $R_m(\theta)$ is the position of the minimum, $\epsilon_m(\theta)$, of the XC potential for given θ. In principle R_m, and hence, S, depends upon ξ, but in order to avoid un-needed complexity in the model, this dependence is neglected, as its effect on the potential energy in the region of interest is small and is absorbed into other parts of the model. As usual in the XC model, the values of $R_m(\theta)$, and hence of $S=S(\theta)$, are determined iteratively once the rest of the potential has been specified.

The initial 3D XC model PES, denoted XC0(3D), is defined by Eqs. (1)–(6), with $F(R,\theta,\xi)$ set to unity. The Heitler–London energy is represented by Eq. (4), with fitting parameters provided in Table A.1 of Ref. 50, while the C_n coefficients are obtained from Eq. (2) using the stretching-dependent coefficients $C_n^{(l)}(\xi)$ obtained from Eq. (3) and the data given in Tables A.2 and A.3 of Ref. 50. The damping functions f_n are given by Eq. (5) (values for the coefficients A_n, B_n, and D_n can be found in Table A.4 of Ref. 50), and the correction function G_{10} is given by Eq. (6).

The present study employs both a 2D PES obtained, as elsewhere,[30,34] for the CO bond length fixed at r_e, its experimental equilibrium value, in Eqs. (1)–(3), and a 2D PES obtained via vibrational averaging of the full 3D PES over the CO ground vibrational state. The PES corresponding to r fixed at r_e is referred to herein simply as the 2D $\mathrm{XC0}_{r=r_e}$ Ne–CO PES, while the 2D PES obtained by averaging the 3D XC0 PES over the CO ground vibrational state (characterized by vibrational quantum number $v_{\mathrm{CO}}=0$) will be referred to as the 2D $\overline{\mathrm{XC0}}_{v_{\mathrm{CO}}=0}$ PES. A slightly modified procedure is employed to determine a PES for Ne–CO dimers in which the CO molecules are in their first excited vibrational states, i.e., for $v_{\mathrm{CO}}=1$. Note that because $E_{\mathrm{int}}(R,\theta,\xi)$ has been represented in the form of a power series in ξ, vibrationally averaged PESs are obtained simply by the replacement of powers of ξ by their averages over the appropriate CO vibrational state, i.e., $\xi^n \rightarrow \langle v_{\mathrm{CO}}|\xi^n|v_{\mathrm{CO}}\rangle$, $n=0,1,2,\ldots$, in Eqs. (1)–(3).

B. Determination of a rigid-rotor 2D model XC(fit) Ne–CO PES

The 2D $\mathrm{XC0}_{r=r_e}$ Ne–CO PES obtained by fixing r at r_e (equivalently, $\xi_e\equiv-0.000\,370\,6$) in the 3D model XC0 PES described in Sec. II A provides a good starting point for the determination of a reliable 2D $\mathrm{XC(fit)}_{r=r_e}$ Ne–CO PES. The relevant coefficients for the 2D $\mathrm{XC0}_{r=r_e}$ PES are given in Appendix A of Ref. 50, and values for the relevant parameters can be found in Tables A.1 and A.5 of that document.

The 2D $\mathrm{XC0}_{r=r_e}$ PES has been employed to compute the frequencies associated with the centers of gravity of the sets of MW hyperfine-structure lines[24] associated with the nine *a*-type transitions[58] for the $^{20}\mathrm{Ne}-^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog. The re-

TABLE I. Comparison between calculated and experimental values for the frequencies of MW transitions in the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog of Ne–CO($v_{\mathrm{CO}}=0$) (units: cm^{-1}). Asymmetric top energy levels are designated by $J_{K_aK_c}$, with J the total molecular angular momentum quantum number and K_a and K_c the asymmetric top labels (Ref. 58).

Transition	$\mathrm{XC0}_{r=r_e}$	$\mathrm{XC(fit)}_{r=r_e}$	Expt.[a]	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$	SAPT[b]	SAPT(S)[b]
1_{01}-0_{00}	0.2265	0.217 42	0.217 41	0.217 39	0.2178	0.2196
2_{02}-1_{01}	0.4527	0.434 52	0.434 51	0.434 47	0.4358	0.4388
3_{03}-2_{02}	0.6783	0.650 99	0.651 00	0.650 92	0.6529	0.6574
4_{04}-3_{03}	0.9027	0.866 50	0.866 54	0.866 42	0.8690	0.8750
2_{12}-1_{11}	0.4422	0.416 59	0.416 66	0.416 61	0.4201	0.4235
3_{13}-2_{12}	0.6628	0.624 23	0.624 26	0.624 26	0.6296	0.6347
4_{14}-3_{13}	0.8828	0.831 05	0.830 98	0.831 11	0.8384	0.8451
2_{11}-1_{10}	0.4735	0.446 04	0.446 03	0.446 00	0.4502	0.4524
3_{12}-2_{11}	0.7046	0.668 30	0.668 32	0.668 25	0.6746	0.6779

[a] Reference 24.

[b] Reference 30.

sults of these calculations for this PES are presented in Table I; all transitions in this table originate from the true ground vibrational level of the dimer. Also presented in this table are the values calculated using the present 2D $\mathrm{XC(fit)}_{r=r_e}$ and $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PESs (see below) and the values obtained for the *ab initio* and scaled SAPT PESs,[30] referred to herein as the SAPT PES and SAPT(S) PES pair [in which "pair" refers to two SAPT(S) PESs, one for Ne–CO($v_{\mathrm{CO}}=0$) dimers and the other for Ne–CO($v_{\mathrm{CO}}=1$) dimers], respectively. Results based upon the S2 PES have not been included in this table, however, because the MW transition frequencies calculated from it differ significantly from experiment.[34]

The energies of the bound levels of the Ne–CO dimer needed for obtaining the MW frequencies have been computed using the TRIATOM code suite of Tennyson *et al.*[59] The notation used to specify the rotational states of the dimer and the MW transitions are those used traditionally in MW spectroscopy[58] and are also employed in Ref. 24. The predicted line positions obtained from the $\mathrm{XC0}_{r=r_e}$ PES overestimate the experimental values of Walker *et al.*[24] typically by 4%–6%. This poor level of agreement between the center-of-gravity frequencies computed from the $\mathrm{XC0}_{r=r_e}$ PES and experiment necessitates a refinement to produce the $\mathrm{XC(fit)}_{r=r_e}$ PES for Ne–CO.

It has often not been necessary, either here or in previous studies,[7–15] to include explicit functional dependencies of the Heitler–London prefactor F upon either R and/or ξ in obtaining XC(fit) model PESs. Hence, an appropriate refinement for Ne–CO has been carried out by introducing adjustable parameters d_l via

$$F(R,\theta,\xi) \equiv F(\theta) = \sum_{l=0}^{l_{\max}} d_l P_l(\cos\theta) \tag{7}$$

and by making small adjustments to the partial-wave components of the multipolar interaction coefficients $C_n^{(l)}$ but with the fitting process constrained so that the long-range coefficients are considered to be adjustable only within their estimated uncertainties (as given in the Appendix[50]). In the following, the results of these latter adjustments are represented by the scaling factors $Q_n^{(l)} = C_n^{(l)}(\text{fitted})/C_n^{(l)}(\text{initial})$, with the $C_n^{(l)}(\text{initial})$ being the starting values found in Table A.5 of Ref. 50.

For the $\mathrm{N_2}$–Ne, Ar, Kr interactions, recommended XC potential surfaces were constructed[10–12] by fitting potential parameters to the frequencies of a few MW transitions for one or two $\mathrm{N_2}$-Rg isotopologs and to a set of reliable interaction second virial coefficient data. That procedure resulted in state-of-the-art PESs for those interactions that provided very good agreement not only with all experimental MW transitions for *all* $\mathrm{N_2}$-Rg isotopologs but also with available experimental data for an extensive set of binary mixture observables. For the present case of the Ne–CO complex, in the absence of extensive second virial coefficient data, all nine experimentally available MW transition frequencies[24] for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog have been utilized for the refinement of the 2D $\mathrm{XC0}_{r=r_e}$ potential parameters to give the $\mathrm{XC(fit)}_{r=r_e}$ PES for the Ne–CO interaction.

The first step, as usual, is to assess the sensitivity of the computed properties, in the present case the set of nine experimentally accessible MW transition frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog, to changes in the values of the individual parameters characterizing the Ne–CO PES. Initial changes in the isotropy parameters d_0 and $C_n^{(0)}$ (for $n>6$ only, as $C_6^{(0)}$ has a rather tight bound on its uncertainty) were made simultaneously to improve the level of agreement with the experimental MW frequencies for the first four transitions listed in Table I. Additional changes were then made, mainly in the anisotropy parameters d_l and $C_n^{(l)}$ ($n>6$, $l\neq 0$) in order to improve the level of agreement with the MW data for the other five transitions employed for the fit. This procedure was iterated and, in the final stages, small changes in both isotropy and anisotropy parameters were required to fit all nine MW frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog to within 0.015%. This level of agreement was achieved by setting $l_{\max}=4$ in Eq. (7), with the coefficients d_i for the $\mathrm{XC(fit)}_{r=r_e}$ PES as given in Table A.6 of Ref. 50, and by minor scalings of the multipolar interaction coefficients $C_n^{(l)}$ in Eq. (4), as given by the factors $Q_n^{(l)}(r=r_e)$ listed in Table A.5 of Ref. 50.

The angular dependence of $R_m(\theta)$, and hence also of

TABLE II. Comparison between calculated and experimental values for the frequencies of MMW transitions in the ^{20}Ne–^{12}C^{16}O isotopolog of Ne–CO($v_{\mathrm{CO}}=0$) (units: cm^{-1}). The traditional *P*-, *Q*-, *R*-branch notation (Ref. 58) is used in this table rather than the asymmetric top notation utilized in Table I.

		Difference $\Delta \equiv \bar{\nu}_{\mathrm{calc}} - \bar{\nu}_{\mathrm{expt}}$ (cm^{-1})			
Transition	Expt.[a]	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}=0}}$	$\mathrm{XC(fit)}_{r=r_e}$	SAPT[b]	SAPT(S)[b]
$P(2)$	2.772 68	−0.002 67	−0.012 93	0.1813	−0.0339
$Q(1)$	3.221 89	−0.002 74	−0.012 89	0.1830	−0.0298
$Q(2)$	3.233 42	−0.002 70	−0.012 90	0.1859	−0.0277
$Q(3)$	3.250 74	−0.002 70	−0.012 91	0.1903	−0.0245
$Q(4)$	3.273 88	−0.002 68	−0.012 91	0.1964	−0.0201
$Q(5)$	3.302 90	−0.002 63	−0.012 89	0.2043	−0.0144
$Q(6)$	3.337 82	−0.00254	−0.012 85	0.2139	−0.0073
$Q(7)$	3.378 70	−0.002 38	−0.012 75	0.2255	0.0015
$Q(8)$	3.425 54	−0.002 13	−0.012 58	0.2294	0.0122
$Q(9)$	3.478 35	−0.001 75	−0.012 29	0.2557	0.0250
$Q(10)$	3.537 05	−0.001 18	−0.011 86	0.2747	0.0404
$Q(11)$	3.601 51	−0.000 37	−0.011 23	0.2967	0.0586
$Q(12)$	3.671 41	0.000 77	−0.010 32	0.3221	0.0803
$Q(13)$	3.746 25	0.002 36	−0.009 05	0.3513	0.1060
$Q(14)$	3.825 16	0.004 53	−0.007 30	0.3847	0.1364
$R(0)$	3.424 61	−0.002 74	−0.012 93	0.1830	−0.0275
$R(1)$	3.623 85	−0.002 76	−0.012 99	0.1860	−0.0228
$R(2)$	3.813 59	−0.002 73	−0.013 03	0.1900	−0.0167
$R(3)$	3.993 58	−0.002 52	−0.012 95	0.1956	−0.0090
$R(4)$	4.163 53	−0.002 03	−0.012 64	0.2029	0.0006
$R(5)$	4.323 16	−0.001 07	−0.011 92	0.2126	0.0124
$R(6)$	4.472 13	0.000 58	−0.010 61	0.2253	0.0268
$R(7)$	4.609 94	0.003 25	−0.008 37	0.2419	0.0447
$R(8)$	4.736 03	0.007 28	−0.004 90	0.2631	0.0668
$R(9)$	4.849 48	0.013 25	0.000 35	0.2904	0.0943
$R(10)$	4.948 96	0.021 88	0.008 05	0.3253	0.1288

[a] References 25–27.

[b] Reference 30.

$S(\theta)$, employed in Eqs. (5) and (6) through $S=7.82a_0/R_m$ for the final 2D $\mathrm{XC(fit)}_{r=r_e}$ PES can be represented explicitly as

$$R_m^{\mathrm{XC(fit)}}(\theta) = \sum_{l=0}^{6} t_l P_l(\cos\,\theta). \tag{8}$$

Specific values for the t_l coefficients for the $\mathrm{XC(fit)}_{r=r_e}$ PES can be found in Table A.6 of Ref. 50. The dependence of R_m, and hence of S, on θ introduces anisotropy into the damping and corrector functions.

To test the ability of the $\mathrm{XC(fit)}_{r=r_e}$ PES to predict quantities that were not included in its determination, the TRIATOM code suite[59] was employed to calculate the transition frequencies of the MMW lines observed in Refs. 25–27. As can be seen from Table II, the calculated values generally lie between 0.2% and 0.5% below the experimental values, which may be compared with an average absolute deviation of about 0.004% for the MW lines (see Table I). This deterioration of the ability of the $\mathrm{XC(fit)}_{r=r_e}$ PES to predict the MMW transition frequencies reliably suggests that it is likely appropriate to modify the refinement procedure so that a few MMW frequencies are also included in it.

As all MW and MMW transitions for the various Ne–CO isotopologs originate from the ground vibrational level of the dimer, they must specifically involve Ne–CO dimers in which the vibrational state of the CO molecule does not change, and the PES utilized for the calculation of these transition frequencies should directly reflect this fact. Moreover, as the mid-IR transitions reported in Refs. 28 and 29 also involve dimers in which the CO molecules are vibrationally excited, two different PESs are required in principle for the calculation of these transition frequencies. 2D PESs obtained by averaging a stretching-dependent 3D PES over appropriate vibrational CO wave functions can provide the required connections. Moreover, in principle, the PES constructed via the vibrational-averaging procedure should be considerably more appropriate for Ne–CO dimers formed from vibrationally excited CO molecules. The determination of 2D XC PESs appropriate to dimers containing CO molecules in their ground and first excited vibrational states is described below.

C. Determination of 2D vibrationally averaged XC(fit) Ne–CO PESs

A process similar to that described in Sec. II B for constructing the 2D $\mathrm{XC(fit)}_{r=r_e}$ PES has been employed to obtain a vibrationally averaged 2D XC PES for Ne–CO dimers in which the CO molecule is in its ground vibrational state.

An initial XC0 PES, denoted by $\overline{\mathrm{XC0}}_{v_{\mathrm{CO}}=0}$ and obtained from the 3D XC0 PES by replacing the powers of ξ in Eqs. (3) and (4) by their averages (as given in Table A.1 of

Ref. 50) over the ground vibrational state of the CO molecule, was then refined to provide excellent agreement with MW data in the same manner that was employed in determining the $\mathrm{XC(fit)}_{r=r_e}$ PES. The resultant PES is very similar to the $\mathrm{XC(fit)}_{r=r_e}$ PES, and hence no additional details of its construction or of results obtained from it need be presented. When this vibrationally averaged PES was employed to calculate the transition frequencies of the MMW lines observed in Refs. 25–27, the calculated frequencies underestimate, in much the same way as those obtained using the $\mathrm{XC(fit)}_{r=r_e}$ PES (see Table II), the corresponding experimental values by up to 0.5%. This level of agreement is markedly poorer than that achieved for the MW data[24] using the same PESs. All the MMW transitions in Table II originate from the true ground vibrational level of the $\mathrm{Ne-CO}(v_{\mathrm{CO}}=0)$ dimer.

Because vibrationally averaged PESs inherently hold greater promise for the computation of mid-IR transition frequencies, a further refinement of the vibrationally averaged PES was carried out to improve agreement with the MMW data. This additional refinement to obtain a final 2D vibrationally averaged XC PES, denoted $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$, employed a procedure similar to that described for the construction of the $\mathrm{XC(fit)}_{r=r_e}$ PES in Sec. II B, except that instead of employing nine MW transitions, a total of seven transitions, consisting of four MW lines (1_{01}-0_{00}, $2_{02}-1_{01}$, 2_{12}-1_{11}, 2_{11}-1_{10}) and three MMW lines (1_{11}-0_{00}, 1_{10}-1_{01}, 1_{11}-2_{02}) of the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog, were utilized in the fitting procedure. The vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES gives slightly poorer agreement (0.01% versus 0.005% on average) with the four experimental MW frequencies employed in the fit while simultaneously improving the agreement (0.09% versus 0.41% on average) with the three MMW frequencies employed in the fit. The full set of MW and MMW transition frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog obtained using the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES can be found in Tables I and II; analogous results obtained with other PESs have also been included in these tables for comparison. The relevant coefficients for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES are as defined in Appendix A of Ref. 50 and are provided in Tables A.1, A.5, and A.6 of that reference; the parameters t_l required to obtain the angular dependence of R_m for this PES via Eq. (8) can also be found in Table A.6 of Ref. 50.

The experimental mid-IR transitions[28,29] for Ne–CO dimers strictly involve two PESs, one for the lower spectroscopic state, in which the dimers contain CO molecules in their ground vibrational ($v_{\mathrm{CO}}=0$) state, and the other for the upper spectroscopic state, in which the dimers contain CO molecules in their first excited ($v_{\mathrm{CO}}=1$) vibrational state. Following the line of reason that led to the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES, an appropriate vibrationally averaged PES for $\mathrm{Ne-CO}(v_{\mathrm{CO}}=1)$ dimers is determined by performing a vibrational averaging of the ξ dependence of the 3D XC0 PES over the first CO excited vibrational state, followed by a refinement of potential parameters to provide an acceptable level of agreement with a set of experimental MW and/or MMW transition frequencies for $\mathrm{Ne-CO}(v_{\mathrm{CO}}=1)$ dimers. However, as no MW or MMW lines have been directly observed for $\mathrm{Ne-CO}(v_{\mathrm{CO}}=1)$ dimers due to the very small population of $v_{\mathrm{CO}}=1$ molecules in a typical sample cell, such a direct fitting procedure cannot readily be carried out. A reasonable vibrationally averaged PES for these dimers should nonetheless be obtainable from the current 3D XC0 PES by replacing powers of ξ by their vibrationally averaged values (as given in Table A.1 of Ref. 50) for $\mathrm{CO}(v_{\mathrm{CO}}=1)$ and retaining the scaling parameter values obtained for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES. The resultant PES is denoted $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$; the relevant potential coefficients have been defined in Appendix A of Ref. 50, and values for them are provided in Tables A.1, A.5, and A.6 of that reference; the parameters t_l required to obtain the angular dependence of R_m, as given by Eq. (8), for this PES are essentially the same as those obtained for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES and can be found in Table A.6 of Ref. 50.

Mid-IR transition frequencies can be obtained (see Sec. IV C) by taking appropriate differences between energy levels computed for the upper spectroscopic state using the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES (and the CO rotational constant for $v_{\mathrm{CO}}=1$) and for the lower spectroscopic state using the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES (and the CO rotational constant for $v_{\mathrm{CO}}=0$); because the PESs involved in these calculations are 2D surfaces, the experimentally determined[60] vibrational frequency, $\bar{\nu}_{\mathrm{CO}}=2143.2712\ \mathrm{cm}^{-1}$, for an isolated CO molecule is added to the differences to produce the final mid-IR frequencies. Comparison of these calculated frequencies with the corresponding experimental frequencies will be made in Sec. IV.

III. DIRECT COMPARISON OF FEATURES OF THE XC(FIT) POTENTIAL ENERGY SURFACES WITH PREVIOUS NE–CO POTENTIAL SURFACES

The $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES for Ne–CO gives rise to a bent equilibrium geometry that corresponds to a global energy minimum $D_e=-49.41\ \mathrm{cm}^{-1}$ ($-225.11\ \mu E_{\mathrm{h}}$) at $(R_e,\theta_e)=(6.395a_0,88.01°)$. The linear Ne–OC geometry ($\theta=180°$) is lower in energy ($\epsilon_m=-41.97\ \mathrm{cm}^{-1}$ at $R=7.023a_0$) than the linear Ne–CO geometry ($\epsilon_m=-26.31\ \mathrm{cm}^{-1}$ at $8.194a_0$), so that there is a higher barrier for rotation about the carbon end than about the oxygen end of the CO moiety. The $\mathrm{XC(fit)}_{r=r_e}$ NeCO PES has potential features that are very similar to those of the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ NeCO PES (see Table III). Features for the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES have also been included in this table. As can be inferred from the coefficients given in Tables A.1 and A.5 of Ref. 50, its features are similar to those of the $\mathrm{XC(fit)}_{r=r_e}$ and $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PESs; in particular, it has a deeper potential well.

The equilibrium well depth D_e and the equilibrium values R_e and θ_e of R and θ obtained for the XC(fit) PESs are compared with those obtained for the SAPT,[30] SAPT(S),[30] and S2 (Ref. 34) PESs in Table III. It can be seen from this table that, on the one hand, the XC(fit) PESs give values for D_e and R_e that are very similar to those obtained by McBane and Cybulski[34] for the S2 PES but differing from the corresponding values obtained by Moszynski *et al.*[30] for the SAPT and SAPT(S) PESs; on the other hand, the XC(fit) PESs give values for θ_e that are close to the values obtained with the SAPT and SAPT(S) PESs but differ from the θ_e value for the

TABLE III. Representative features of the Ne–CO PESs.

	PES					
Feature	$\mathrm{XC(fit)}_{r=r_e}$	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$	$\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$	S2[a]	SAPT[b]	SAPT(S)[b]
D_e (cm^{-1})	−49.41	−49.41	−49.55	−48.50	−53.49	−54.48
R_e (a_0)	6.390	6.395	6.401	6.396	6.337	6.316
θ_e (deg)	88.26	88.01	87.29	99.85	87.80	87.80
$\epsilon_m(0)$ (cm^{-1})	−26.59	−26.31	−26.42	−32.48	−28.16	−27.54
$R_m(0)$ (a_0)	8.174	8.194	8.200	8.085	8.209	8.238
$\sigma(0)$ (a_0)	7.413	7.432	7.439	7.336	7.466	7.494
$\epsilon_m(90)$ (cm^{-1})	−49.38	−49.37	−49.48	−47.80	−53.31	−54.29
$R_m(90)$ (a_0)	6.379	6.383	6.386	6.430	6.329	6.308
$\sigma(90)$ (a_0)	5.659	5.662	5.663	5.707	5.616	5.595
$\epsilon_m(180)$ (cm^{-1})	−42.07	−41.97	−42.14	−44.48	−49.26	−48.15
$R_m(180)$ (a_0)	7.012	7.023	7.030	6.997	6.936	6.962
$\sigma(180)$ (a_0)	6.351	6.361	6.368	6.319	6.280	6.303
$\Delta\epsilon_m$ (cm^{-1})	−15.48	−15.65	−15.72	−12.00	−21.10	−20.61
ΔR_m (a_0)	−1.162	−1.171	−1.170	−1.089	−1.273	−1.276
$\Delta\sigma$ (a_0)	−1.062	−1.071	−1.072	−1.016	−1.185	−1.191
Features of the isotropic components						
ϵ_{0m} (cm^{-1})	−33.20	−33.26	−33.38	−33.41	−34.42	−34.12
R_{0m} (a_0)	7.143	7.146	7.150	7.178	7.166	7.177
σ_0 (a_0)	6.401	6.404	6.408	6.431	6.425	6.436

[a] Reference 34.

[b] Reference 30.

S2 PES. Note that the SAPT PES and the SAPT(S) PES have 10% deeper wells than either the XC(fit) PESs or the S2 PES.

For van der Waals complexes formed from homonuclear diatomic molecules and noble gas atoms the differences $\Delta\epsilon_m$, ΔR_m, and $\Delta\sigma$ (σ is the distance at which the interaction energy vanishes) between the values of these features for the perpendicular geometry (normally the equilibrium geometry) and the linear geometry have often been employed to represent the anisotropy of the PES in the region of the global minimum. For van der Waals complexes formed with a heteronuclear diatomic molecule such as CO, however, the two linear geometries have significantly different energies and the global minimum is generally displaced from 90°, so that differences between these features at 90° and either of the linear geometries is no longer as meaningful as it is for complexes involving homonuclear diatomic molecules. For this reason, it seems more useful to characterize the anisotropies in these features of the PES by the differences between their values for the two linear geometries of the complex: These differences are also presented in Table III, with Δ designating the value of the potential feature at $\theta=180°$ minus its value at $\theta=0°$.

On the one hand the SAPT PES,[30] and especially the scaled SAPT(S) PES pair,[30] gives much better agreement with the Ne–CO spectroscopic data of Refs. 24–29 than does the S2 PES,[34] while on the other hand the S2 PES gives[61] better agreement with bulk gas virial data[62,63] and molecular beam scattering data,[35,36] especially so for the state-to-state differential cross section data of Ref. 36 than does the SAPT or SAPT(S) PESs.[34–36] McBane and Cybulski[34] concluded from their comparisons between theory and experiment that a more realistic PES should be shallower than the SAPT PES but not as shallow as the S2 PES, while Lorenz *et al.*[36] reasoned that a more realistic PES should have anisotropies lying somewhere between those exhibited by the SAPT and S2 PESs. As can be seen from Table III, all three of the present XC model PESs have global minima that lie between those of the SAPT and S2 PESs. Moreover, the characteristic differences $\Delta\epsilon_m$ in the depths of the 2D XC PESs lie between the differences for the SAPT PESs and the S2 PES, as do the characteristic differences, ΔR_m and $\Delta\sigma$, for the distances at which the minimum and the zero interaction occur for $\theta=0°$ and 180°. Based upon all three of these criteria, the 2D XC PESs are more anisotropic than the S2 PES but less anisotropic than the SAPT and SAPT(S) PESs. The model XC PESs thus satisfy both of the broad criteria required to be able to provide accurate values for spectroscopic properties, as shown herein, and for molecular beam scattering cross sections and bulk gas properties.[64]

All three types of anisotropy in the PES will influence the MW, MMW, and IR spectra of a Ne–CO van der Waals dimer. Molecular beam scattering cross sections, bulk gas transport properties, and bulk gas relaxation phenomena, however, are relatively insensitive to anisotropy in ϵ_m, only slightly sensitive to anisotropies in R_m and σ, and most sensitive to the anisotropy higher up on the repulsive wall of the PES.

Table III also gives values for the depth ϵ_{m0} and position R_{m0} of the minimum energy for the spherical component, $V_0(R)$, for each PES, plus the position σ_0 at which each

$V_0(R)$ vanishes. The potential features of $V_0(R)$ for the three XC PESs are all quite similar (with ϵ_{0m} values differing by less than 0.6% and R_{0m} and σ_0 values typically differing by about 0.1%) but differ more significantly from the corresponding features of the SAPT and S2 PESs (by as much as 3.7% for ϵ_{0m} and about 0.5% for R_{0m} and 0.6% for σ_0).

IV. ENERGY LEVELS, MICROWAVE, MILLIMETER-WAVE, AND MID-IR SPECTRA FOR THE NE–CO ISOTOPOLOGS

High-resolution MW, MMW, and IR spectra provide excellent probes of intermolecular interactions, especially in the vicinity of the global minimum of the PES. MW transitions for seven Ne–CO isotopologs have been reported by Walker *et al.*,[24] while MMW spectra have been obtained for three Ne–CO isotopologs by Winnewisser *et al.*,[25] Roth *et al.*,[26] and Surin *et al.*,[27] and mid-IR spectra have been obtained by Randall *et al.*[28] for both the $^{20}\text{Ne}-{}^{12}\text{C}^{16}\text{O}$ and $^{22}\text{Ne}-{}^{12}\text{C}^{16}\text{O}$ isotopologs, while additional mid-IR frequencies have been reported for the $^{20}\text{Ne}-{}^{12}\text{C}^{16}\text{O}$ isotopolog by McKellar and Chan.[29]

A. Calculation of relevant energy levels and transition frequencies

Bound energy levels for the Ne–CO van der Waals complex have been calculated by the variational method using the TRIATOM code suite of Tennyson *et al.*[59] and taking into account off-diagonal Coriolis terms. The present calculations employed a radial basis of 40 Morse-oscillator functions parametrized by the equilibrium distance R_e, the dissociation energy D_e, and the fundamental vibrational frequency ω_e. Optimization of these three parameters was attained by minimizing the energy of the $J=0$ state to give $R_e=7.2a_0$, $D_e=157\ \mu E_\text{h}$, and $\omega_e=75\ \mu E_\text{h}$, all three values being essentially the same as those employed by Moszynski *et al.*[30] in their calculations for the SAPT PES. In addition to the basis-set parameters, carbon monoxide rotational constants[30] $B_0=1.922\,516\,5\ \text{cm}^{-1}$ and $B_1=1.905\,013\,5\ \text{cm}^{-1}$, respectively, have also been employed for calculations involving Ne–CO van der Waals complexes formed with CO in its ground ($v_\text{CO}=0$) and first excited ($v_\text{CO}=1$) vibrational states, respectively. Both the $\overline{\text{XC(fit)}}_{v_\text{CO}=0}/\overline{\text{XC}}_{v_\text{CO}=1}$ and SAPT(S) PES pairs give (slightly) different PESs for Ne–CO dimers with CO in its ground ($v_\text{CO}=0$) and first excited ($v_\text{CO}=1$) vibrational states; eigenvalue calculations involving the $\text{XC(fit)}_{r=r_e}$ PES employ precisely the same PES for both the $\text{Ne}-\text{CO}(v_\text{CO}=0)$ and $\text{Ne}-\text{CO}(v_\text{CO}=1)$ dimers along with the appropriate rotational constants. Calculations for the predominant Ne–CO isotopolog employed constituent atom masses,[65] $m(^{20}\text{Ne})=19.9924$ amu, $m(^{12}\text{C})=12.0$ amu, and $m(^{16}\text{O})=15.994\,91$ amu; masses for constituent atoms in other Ne–CO isotopologs were also taken from Ref. 65 in order to facilitate comparisons between the present results and those of Refs. 30 and 34.

Bound state energies for each isotopolog have been obtained for total angular momentum values J ranging from 0 to $J_\text{max}\leq 16$. For the $^{20}\text{Ne}-{}^{12}\text{C}^{16}\text{O}$ complex, the ground vibrational energies obtained by employing the $\text{XC(fit)}_{r=r_e}$ and $\overline{\text{XC(fit)}}_{v_\text{CO}=0}$ PESs are -31.5870 and $-31.7514\ \text{cm}^{-1}$, respectively, which correspond to zero-point energies of 17.827 and 17.656 cm^{-1}, respectively. These zero-point energies may be compared with the values of 21.341 cm^{-1} obtained for the SAPT PES by Moszynski *et al.*[30] and 17.406 cm^{-1} obtained for the S2 PES by McBane and Cybulski.[34] The first excited Ne–CO dimer state with $J=0$ (namely, the state with $v_\text{CO}=0$, $J=0$, and $v_b=1$) corresponds to a bending excitation of the Ne–CO dimer that can be correlated with the hindered rotation of the CO moiety in the Ne–CO potential well; this state, lying at $-23.1685\ \text{cm}^{-1}$, is 8.58 cm^{-1} above the ground state energy for the $\overline{\text{XC(fit)}}_{v_\text{CO}=0}$ PES. The bending excitation energy of 8.58 cm^{-1} obtained with the present $\overline{\text{XC(fit)}}_{v_\text{CO}=0}$ PES [(versus 8.56 cm^{-1} for the $\text{XC(fit)}_{r=r_e}$ PES] is in excellent agreement with the experimental value of 8.58 cm^{-1} reported by McKellar and Chan;[29] the corresponding values of 8.25 cm^{-1} for the *ab initio* SAPT PES [cf. 8.51 cm^{-1} for the SAPT(S) PES] and 8.36 cm^{-1} for the *ab initio* S2 PES can be deduced from the calculations reported by Moszynski *et al.*[18] and by McBane and Cybulski.[34] The bending frequency of 8.58 cm^{-1} for ground state Ne–CO, obtained using the $\overline{\text{XC(fit)}}_{v_\text{CO}=0}$ PES, decreases slightly to 8.46 cm^{-1} upon excitation of the CO stretch, as obtained from the $\overline{\text{XC}}_{v_\text{CO}=1}$ PES, and is in good agreement with the corresponding experimental value[28,29] of 8.49 cm^{-1} for the bending frequency of Ne–CO in the $v_\text{CO}=1$ state; the corresponding value for the SAPT(S) PES is 8.42 cm^{-1}.

B. Microwave and millimeter-wave transitions

As has been pointed out in Ref. 30, the only truly conserved quantum numbers for a weakly bound van der Waals complex such as the Ne–CO dimer are the total angular momentum quantum number J and the (spectroscopic) parity quantum number $\sigma\equiv p(-1)^J$, in which p is the conventional parity quantum number. Moreover, both the quantum number j associated with the end-over-end rotational motion of a free molecule and the quantum number K ($\equiv K_a$) associated with the projection of the molecular species rotational angular momentum vector $\mathbf{j}$ onto the interspecies axis are approximately conserved. States for which $K=0,\pm 1,\pm 2,\ \ldots$ are correspondingly denoted by $\Sigma,\Pi,\Delta,\ldots$; values of the spectroscopic parity quantum number σ are traditionally designated by superscripts e (for $\sigma=+1$) and f (for $\sigma=-1$). The notation used to specify the rotational states of the complex and the specific MW transitions are those used traditionally in the MW spectroscopy of asymmetric top molecules.[58]

The MW and MMW spectral transitions all correspond to pure end-over-end rotational transitions in the $\text{Ne}-\text{CO}(v_\text{CO}=0)$ van der Waals dimers. The distinction between these two types of transition is provided by the spectroscopic selections rules. Specifically, the MW transitions typically correspond to spectroscopic selection rules $\Delta K_a=0$ and $\Delta K_c=\pm 1$ and are traditionally referred to as "a-type" transitions, while the MMW transitions typically correspond to spectroscopic selection rules $\Delta K_a=\pm 1$ and $\Delta K_c=\pm 1$ and are traditionally referred to as "b-type" transitions.[58]

As has been seen in Table I, the relative absolute differ-

TABLE IV. RMSD values for the computation of MW and MMW transition frequencies for the Ne–CO($v_{\mathrm{CO}}=0$) isotopologs (units: cm^{-1}). $\Delta_{\min}$ and $\Delta_{\max}$ are the minimum and maximum absolute deviations for a given set of spectroscopic lines.

			$\mathrm{XC(fit)}_{r=r_e}$	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$			SAPT(S)[a]
Type	Isotopolog	No. of lines	RMSD	$\Delta_{\min}$	RMSD	$\Delta_{\max}$	RMSD
MW[b]	^{20}Ne–^{12}C^{16}O	9	0.000 036	0.000 004	0.000 072	0.000 126	0.0083
	^{20}Ne–^{13}C^{16}O	4	0.000 014	0.000 025	0.000 089	0.000 141	0.0058
	^{20}Ne–^{13}C^{17}O	2	0.000 024	0.000 049	0.000 079	0.000 101	0.0034
	^{20}Ne–^{13}C^{18}O	4	0.000 122	0.000 070	0.000 207	0.000 310	0.0056
	^{21}Ne–^{12}C^{16}O	3	0.000 005	0.000 021	0.000 053	0.000 076	0.0045
	^{22}Ne–^{12}C^{16}O	4	0.000 015	0.000 021	0.000 072	0.000 112	0.0055
	^{22}Ne–^{13}C^{16}O	4	0.000 012	0.000 026	0.000 087	0.000 136	0.0055
	All MW	30	0.000 017	0.000 004	0.000 097	0.000 310	0.0060
MMW[c]	^{20}Ne–^{12}C^{16}O	26	0.011 422	0.000 370	0.005 696	0.021 883	0.0557
	^{21}Ne–^{12}C^{16}O	10	0.012 673	0.001 978	0.002 391	0.002 515	0.0227
	^{22}Ne–^{12}C^{16}O	21	0.011 990	0.000 353	0.001 863	0.002 313	0.0290
	All MMW	57	0.011 874	0.001 978	0.004 109	0.004 528	0.0423
	All MW and MMW	87	0.009 428	0.000 004	0.003 263	0.004 258	0.0338

[a] Reference 30.
[b] Reference 24.
[c] References 25–27.

ences between calculated and experimental[24] MW frequencies for the ^{20}Ne–^{12}C^{16}O isotopolog are quite small for the two XC(fit) PESs, corresponding typically to percentage differences of less than 0.015%, averaging 0.01% for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES and 0.005% for the $\mathrm{XC(fit)}_{r=r_e}$ PES. As can be seen from Table IV, with the exception of the ^{20}Ne–^{13}C^{18}O isotopolog, these PESs give excellent agreement with all MW data. The RMSD values for the MW transition frequencies calculated from the SAPT(S) PES are on average two orders of magnitude larger than the RMSD values obtained from the XC(fit) PESs.

The ability of the $\mathrm{XC(fit)}_{r=r_e}$ and SAPT(S) PESs to predict MMW transition frequencies can be seen from Table II directly in terms of the differences $\Delta \equiv \bar{\nu}_{\mathrm{calc}} - \bar{\nu}_{\mathrm{expt}}$ for individual MMW transitions in the ^{20}Ne–^{12}C^{16}O isotopolog or, more generally, in terms of RMSD values for the full sets of MW and MMW lines available for different Ne–CO isotopologs in Table IV. As can be seen from Table IV, the $\mathrm{XC(fit)}_{r=r_e}$ PES gives RMSD values for the MMW data that are typically about three orders of magnitude larger than the RMSD values obtained for the MW data. The level of agreement with the MMW experimental data[25–27] is, however, much better than that achievable with the SAPT(S) PES for Ne–CO($v_{\mathrm{CO}}=0$) dimers. The $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES, which was determined bearing in mind both the need for improvement in the predictive ability of a Ne–CO PES with respect to MMW frequencies and the need to calculate mid-IR transition frequencies properly, gives excellent agreement with MMW experimental results for all Ne–CO isotopologs, as can be seen from Table IV. The RMSD value obtained for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES for all 87 pure rotational (MW plus MMW) transitions is a factor of 3 better than that obtained for the $\mathrm{XC(fit)}_{r=r_e}$ PES and is typically an order of magnitude better than the RMSD value for the SAPT(S) PES; no comparisons are presented here for the S2 PES, as it overestimates the MMW data on average by about 10%; it has also been shown[34] to underestimate the MW data on average by about 1.5%.

Even though, as mentioned earlier, no MW or MMW transitions associated with the Ne–CO($v_{\mathrm{CO}}=1$) dimers have been observed experimentally, a set of Ne–CO($v_{\mathrm{CO}}=1$) "experimental" transition frequencies can be extracted from the published[24–29] experimental mid-IR data, plus MW and/or MMW data. For example, for the ^{20}Ne–^{12}C^{16}O isotopolog, the MMW Q-transition "data" for Ne–CO($v_{\mathrm{CO}}=1$) dimers can be obtained from the corresponding data[27] for Ne–CO($v_{\mathrm{CO}}=0$) dimers along with the mid-IR data[28] for the $K=1\leftarrow 0$ and $K=0\leftarrow 1$ subbands via the relation

$$[Q(J)]_{v_{\mathrm{CO}}=1} = [Q(J)]_{K=1\leftarrow 0} - [Q(J)]_{K=0\leftarrow 1} - [Q(J)]_{v_{\mathrm{CO}}=0}.$$

Eleven such experimental MW transition frequencies associated with ^{20}Ne–^{12}C^{16}O($v_{\mathrm{CO}}=1$) dimers are compared in Table V with transition frequencies calculated from the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES. Also shown in this table are values calculated from the SAPT(S) PES for $v_{\mathrm{CO}}=1$ and from the present $\mathrm{XC(fit)}_{r=r_e}$ PES using the rotational constant B_1 associated with the first excited vibrational state of CO. Both the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES and the $\mathrm{XC(fit)}_{r=r_e}$ PES give significantly better agreement (by an order of magnitude) with the experimental values than does the SAPT(S) PES.

In addition to the experimental MW transition frequencies just discussed, a set of 33 experimental MMW transition frequencies for the ^{20}Ne–^{12}C^{16}O($v_{\mathrm{CO}}=1$) dimer have also been extracted from the experimental mid-IR and MMW data. These transition frequencies, together with differences Δ, are shown in Table VI. For the MMW spectra also, the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES and the $\mathrm{XC(fit)}_{r=r_e}$ PES both give significantly better agreement with the data than does the SAPT(S) PES for $v_{\mathrm{CO}}=1$ but in this case only by about a factor of 3. Here,

TABLE V. Comparison between calculated and experimental values for the frequencies of MW transitions associated with the ground bending level of the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}(v_{\text{CO}}=1)$ dimer (units: cm^{-1}).

		Difference $\Delta \equiv \bar{\nu}_{\text{calc}} - \bar{\nu}_{\text{expt}}$ (cm^{-1})		
MW transition	Expt.	$\overline{\text{XC}}_{v_{\text{CO}=1}}$	$\text{XC(fit)}_{r=r_e}$	SAPT(S)
2_{02}-1_{01}	0.4343	−0.0005	0.0002	0.0047
3_{03}-2_{02}	0.6500	−0.0000	0.0010	0.0077
4_{04}-3_{03}	0.8654	−0.0002	0.0011	0.0100
5_{05}-4_{04}	1.0798	−0.0007	0.0009	0.0120
2_{12}-1_{11}	0.4160	−0.0003	0.0005	0.0076
3_{13}-2_{12}	0.6233	−0.0004	0.0008	0.0115
4_{14}-3_{13}	0.8292	−0.0001	0.0017	0.0161
5_{15}-4_{14}	1.0350	−0.0004	0.0016	0.0198
2_{11}-1_{10}	0.4458	−0.0004	0.0003	0.0069
3_{12}-2_{11}	0.6669	−0.0005	0.0015	0.0114
4_{13}-3_{12}	0.8895	−0.0010	0.0002	0.0136
RMSD MW		0.0005	0.0010	0.0118

TABLE VI. Comparison between calculated and experimental values for the frequencies of MMW transitions associated with the ground bending level of the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}(v_{\text{CO}}=1)$ dimer (units: cm^{-1}).

		Difference $\Delta \equiv \bar{\nu}_{\text{calc}} - \bar{\nu}_{\text{expt}}$ (cm^{-1})		
MMW transition	Expt.	$\overline{\text{XC}}_{v_{\text{CO}=1}}$	$\text{XC(fit)}_{r=r_e}$	SAPT(S)
$P(2)$	2.7434	−0.0166	−0.0164	−0.0393
$P(3)$	2.5093	−0.0168	−0.0168	−0.0393
$P(4)$	2.2675	−0.0173	−0.0174	−0.0381
$P(5)$	2.0174	−0.0169	−0.0171	−0.0345
$P(6)$	1.7610	−0.0172	−0.0174	−0.0345
$P(7)$	1.4960	−0.0152	−0.0154	−0.0208
$P(8)$	1.2280	−0.0159	−0.0161	−0.0123
$P(9)$	0.9512	−0.0127	−0.0129	0.0027
$P(10)$	0.6704	−0.0098	−0.0100	0.0205
$P(11)$	0.3856	−0.0065	−0.0070	0.0424
$R(0)$	3.3938	−0.0161	−0.0149	−0.0393
$R(1)$	3.5936	−0.0173	−0.0156	−0.0393
$R(2)$	3.7829	−0.0175	−0.0153	−0.0203
$R(3)$	3.9620	−0.0173	−0.0145	−0.0119
$R(4)$	4.1141	−0.0176	−0.0142	−0.0023
$R(5)$	4.2906	−0.0170	−0.0129	0.0100
$R(6)$	4.4400	−0.0169	−0.0122	0.0239
$R(7)$	4.5770	−0.0145	−0.0093	0.0423
$R(8)$	4.7040	−0.0125	−0.0068	0.0635
$R(9)$	4.8155	−0.0056	0.0005	0.0930
$R(10)$	4.9180	−0.0007	0.0054	0.1247
$R(11)$	5.0005	0.0121	0.0180	0.1697
$Q(1)$	3.1925	−0.0170	−0.0162	−0.0348
$Q(2)$	3.2041	−0.0170	−0.0162	−0.0327
$Q(3)$	3.2208	−0.0163	−0.0155	−0.0288
$Q(4)$	3.2450	−0.0172	−0.0165	−0.0254
$Q(5)$	3.2742	−0.0171	−0.0166	−0.0197
$Q(6)$	3.3103	−0.0180	−0.0176	−0.0136
$Q(7)$	3.3510	−0.0173	−0.0171	−0.0044
$Q(8)$	3.3990	−0.0179	−0.0171	0.0054
$Q(9)$	3.4525	−0.0177	−0.0179	0.0178
$Q(10)$	3.5140	−0.0194	−0.0200	0.0308
$Q(11)$	3.5806	−0.0200	−0.0211	0.0474
RMSD MMW		0.0158	0.0152	0.0489

also the two XC PESs perform quite similarly. Because the characteristic features of the Ne–CO XC PESs are rather similar (see Table III), only relatively small differences can be expected between MW or MMW transition frequencies calculated using them.

C. Midinfrared transitions

Mid-IR transitions in the Ne–CO dimer pertain to transitions in which the lower spectroscopic state belongs to a $\text{Ne}-\text{CO}(v_{\text{CO}}=0)$ dimer and the upper spectroscopic state belongs to a $\text{Ne}-\text{CO}(v_{\text{CO}}=1)$ dimer. The first high-resolution spectroscopic measurements of spectra associated with the Ne–CO van der Waals dimer were in fact mid-IR spectra for the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ and $^{22}\text{Ne}-^{12}\text{C}^{16}\text{O}$ isotopologs obtained by Randall *et al.*[28] in 1993. Additional high precision measurements[29] of the mid-IR spectra for the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ isotopolog were obtained in 1998 to give a total of 350 mid-IR transitions from the ground state of the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ isotopolog plus an additional 91 mid-IR transitions from the ground state of the $^{22}\text{Ne}-^{12}\text{C}^{16}\text{O}$ isotopolog. Fifty-four of the $^{20}\text{Ne}-^{12}\text{C}^{16}\text{O}$ mid-IR transitions are combination bands involving the first excited bending $(v_b=1)$ vibrational level.

Because little can be gained by reporting comparisons between calculated and experimental values for the mid-IR line frequencies on a transition-by-transition basis, comparisons with these spectroscopic data are given here in terms of RMSD values between calculated and experimental values for sets of line frequencies. Comparisons for mid-IR lines involving only the ground bending vibrational level $v_b=0$ is made in Tables VII and VIII, while Table IX gives the comparison for mid-IR lines involving the first excited bending vibrational states of Ne–CO dimers. Minimum and maximum absolute deviations $(\Delta_{\min},\ \Delta_{\max})$ have also been included for the calculations that employ the $\overline{\text{XC(fit)}}_{v_{\text{CO}}=0}$ PES for the lower spectroscopic state and the $\overline{\text{XC}}_{v_{\text{CO}}=1}$ PES for the upper spectroscopic state. These quantities have been included to provide a measure of the span of deviations between calculated and experimentally determined transition frequencies. The only PESs other than the present XC model PESs for which mid-IR results are reported here is the SAPT(S) PES pair of Ref. 30, as the original SAPT PES was specifically modified/scaled to provide improved agreement with the experimental mid-IR frequencies of Ref. 28.

Comparisons between theory and experiment are shown in Tables VII and VIII not only for sets of P-, Q-, and R-branch mid-IR transitions associated with subbands determined by the spectroscopic selection rule $\Delta K \equiv K' - K'' = 0, \pm 1$ but also collectively (in Tables VII and VIII) for the full set of mid-IR data for a given isotopolog and globally (see the final row in Table VIII) for the set of all mid-IR data involving only the ground bending vibrational level of the Ne–CO dimers (characterized by the quantum number $v_b=0$). Energy levels have been calculated for total angular momentum quantum numbers $0 \le J \le J_{\max}(K)$, with $J_{\max}(K)$ having the values 16, 16, 14, and 10 for the e parity states of the $K=0$, 1, 2, and 3 levels, respectively, and $J_{\max}(K)=15$, 14, and 9 for the f parity states of the $K=1$, 2, and 3 levels, respectively. These values determine the number of experimental frequencies with which comparisons can be made.

TABLE VII. Comparisons between calculated and experimental (Refs. 28 and 29). values for the frequencies of spectroscopic mid-IR transitions of the ^{20}Ne$-^{12}$C^{16}O isotopolog that involve the ground bending vibrational level $v_b=0$ (units: cm^{-1}).

			$\mathrm{XC(fit)}_{r=r_e}$	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ plus $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$			SAPT(S)[a]
Subband $K'\leftarrow K''$	Branch	No. of lines	RMSD	$\Delta_{\min}$	RMSD	$\Delta_{\max}$	RMSD
$0\leftarrow 0$	P	15	0.0738	0.0048	0.0077	0.0189	0.0117
	R	15	0.0890	0.0062	0.0089	0.0139	0.0455
$1\leftarrow 0$	P	15	0.0856	0.0042	0.0279	0.0661	0.1459
	R	16	0.1023	0.0060	0.0462	0.1547	0.2249
	Q	13	0.0522	0.0228	0.0245	0.0267	0.0598
$0\leftarrow 1$	P	14	0.0684	0.0029	0.0321	0.0852	0.1004
	R	15	0.0695	0.0006	0.0446	0.1130	0.0999
	Q	11	0.0797	0.0037	0.0045	0.0057	0.0259
$2\leftarrow 1$	Q_{fe}	13	0.0405	0.0179	0.0661	0.1198	0.0637
	Q_{ef}	11	0.2922	0.0105	0.2333	0.5391	0.4837
	R_{ee}	11	0.2670	0.0073	0.2064	0.5151	0.4779
	R_{ff}	13	0.0527	0.0181	0.0438	0.0567	0.0988
$1\leftarrow 2$	Q_{ef}	10	0.1113	0.0006	0.0228	0.0476	0.0760
	Q_{fe}	10	0.1945	0.0315	0.2589	0.5825	0.4668
	P_{ee}	11	0.1784	0.0318	0.2394	0.5637	0.4485
	P_{ff}	13	0.0813	0.0033	0.0184	0.0337	0.0789
$3\leftarrow 2$	Q_{fe}	7	0.0779	0.0185	0.1298	0.2578	0.1318
	Q_{ef}	3	0.3623	0.3645	0.4314	0.4967	0.1899
	R_{ee}	3	0.4832	0.4216	0.5524	0.6779	0.3622
	R_{ff}	3	0.0201	0.0647	0.0740	0.0824	0.0838
$2\leftarrow 3$	Q_{ef}	6	0.1780	0.0048	0.0882	0.1855	0.1855
	Q_{fe}	5	0.4380	0.1415	0.3141	0.4690	0.1862
	P_{ee}[b]	5	0.5306	0.1556	0.4126	0.6532	0.3027
	P_{ff}[b]	5	0.1041	0.0019	0.0129	0.0217	0.0311
All ^{20}Ne$-^{12}$C^{16}O IR lines		243	0.1715	0.0006	0.1513	0.6779	0.2304

[a] Reference 30.

[b] In Table IV of Ref. 29 the e/f labels for the P-branch lines should be switched. Also, for the first P-branch column (correctly labeled f) the data for the $P(8)$ to $P(12)$ transitions should be read as those for the $P(9)$ to $P(13)$ transitions, and the missing $P(8)$ line has the value of 2130.8593 (observed), with a residual of -0.0005 (Ref. 71).

Comparisons involving subbands with $K'=0$ and/or $K''=0$ are made with the data of Ref. 28 and comparisons involving subbands with both K' and K'' nonzero are made with the data of Ref. 29. The $i'i''$ subscripts on particular P-, Q-, and R-branch symbols refer to the spectroscopic parities of the final (i') and initial (i'') states for those specific transitions for which there is more than one possible pair of parity states. Comparisons between columns 4, 6, and 8 of Tables VII and VIII show that, in general, employment of the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES for the lower spectroscopic state together with the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES for the upper spectroscopic state gives significantly better agreement with the mid-IR transition frequencies for the $K=0$ and 1 subbands than is obtained by employing either the $\mathrm{XC(fit)}_{r=r_e}$ PES or the SAPT(S) PES pair. However, the same comparisons for subbands involving $K=2$ and 3 (see Table VII) indicate that while the performance of the vibrationally averaged XC PES pair relative to the SAPT(S) PES pair remains the same as that seen for the $K=0$ and 1 subbands, it performs relatively similarly, on the whole, to the $\mathrm{XC(fit)}_{r=r_e}$ PES. Specific shortcomings of the vibrationally averaged XC PES pair, indicated by an unusually large RMSD value associated with a particular subband, are generally apparent for transitions involving states characterized by e parity and $K=2$ or 3; the RMSD value for these cases is largely associated with states having high values of the total angular momentum J. It is not immediately obvious how to improve the agreement further for these specific sets of transitions without compromising the level of agreement obtained for the other transitions. The final row of Table VII and the final two rows of Table VIII show that the vibrationally averaged XC PES pair gives overall slightly better agreement with the full set of 328 mid-IR transitions than does the $\mathrm{XC(fit)}_{r=r_e}$ PES and significantly better agreement than does the SAPT(S) PES pair.

Table IX presents comparisons between theory and experiment for combination bands in which the first excited dimer bending vibrational levels are involved, specifically with v_b quantum numbers $(v_b',v_b'')=(1,0)$, $(0,1)$, $(1,1)$. The subbands are indicated by $(v_b',K')\leftarrow(v_b'',K'')$. Comparisons for the subband $(1,0)\leftarrow(0,0)$ are with the data of Ref. 28; all other comparisons are with data from Ref. 29. Use of the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair also gives slightly better overall agreement with the full 52 combination-band mid-IR

TABLE VIII. Comparisons between calculated and experimental (Ref. 28) values for the frequencies of spectroscopic mid-IR transitions of the ^{22}Ne–^{12}C^{16}O isotopolog that involve the ground bending vibrational state $v_b=0$ (units: cm^{-1}).

			$\mathrm{XC(fit)}_{r=r_e}$	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ plus $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$			SAPT(S)[a]
Subband $K' \leftarrow K''$	Branch	No. of lines	RMSD	Δ_{min}	RMSD	Δ_{max}	RMSD
$0 \leftarrow 0$	*P*	13	0.0742	0.0056	0.0081	0.0193	0.0114
	R	15	0.0751	0.0023	0.0077	0.0128	0.0503
$1 \leftarrow 0$	*P*	10	0.0926	0.0012	0.0246	0.0500	0.1560
	R	9	0.0701	0.0022	0.0185	0.0240	0.1196
	Q	10	0.0529	0.0211	0.0231	0.0246	0.0473
$0 \leftarrow 1$	*P*	8	0.0714	0.0029	0.0245	0.0496	0.0810
	R	11	0.0725	0.0042	0.0336	0.0784	0.0685
	Q	9	0.0785	0.0032	0.0043	0.0064	0.0250
All ^{22}Ne–^{12}C^{16}O IR lines[b]		85	0.0742	0.0012	0.0199	0.0784	0.0800
All $v_b=0$ IR lines[c]		328	0.1524	0.0006	0.1306	0.6779	0.2025

[a] Reference 30.
[b] Reference 28.
[c] References 28 and 29.

transitions than is obtained for the $\mathrm{XC(fit)}_{r=r_e}$ PES and gives significantly better agreement with these data than is obtained for the SAPT(S) PES pair.

As the mid-IR transitions for which comparisons have been carried out in Tables VII–IX lie in the frequency range 2130 cm$^{-1} \le \bar{\nu} \le 2160$ cm^{-1} characteristic of the fundamental CO stretching frequency, the RMSD values given therein represent differences between theory and experiment of the order of 0.006%–0.013%. The final row of Table IX indicates that the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair provides an overall agreement with experiment that is significantly better than that obtained with the SAPT(S) PES pair and slightly better than that obtained with the (rigid-rotor) $\mathrm{XC(fit)}_{r=r_e}$ PES. The bound levels of the Ne–CO($v_{\mathrm{CO}}=1$) dimers lie slightly deeper in the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ potential well than do the corresponding levels computed from the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES, as can be inferred from the dispersion energy coefficients found in Table A.5 of Ref. 50, giving rise to a redshift of 0.077 cm^{-1} for the CO fundamental band. This calculated redshift, which is not directly observable, can be compared with the experimentally deduced redshift of 0.072 cm^{-1} noted by Randall *et al.*[28] for these transitions and with the value of 0.012 cm^{-1} obtained with the $\mathrm{XC(fit)}_{r=r_e}$ PES (which can be associated with the differences in the rotational constants B_1 and B_0 for CO). The SAPT(S) PES pair of Ref. 30, which was specifically scaled to provide improved agreement with the mid-IR data of Ref. 28, produces a redshift of 0.063 cm^{-1} for these spectral transitions and generally provides a considerable improvement in representing the mid-IR spectra relative to the original *ab initio* SAPT PES. As can be seen from Table II the SAPT(S) PES also gives significantly better agreement with the MMW data of Refs. 25–27 than does the original SAPT PES. Unfortunately, however, agreement with the MW data of Ref. 24 is considerably worsened (see Table I) by the adjustments made to the original SAPT PES in order to achieve the improved agreement with the mid-IR data.

FORTRAN codes for the $\mathrm{XC(fit)}_{r=r_e}$, $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$, and $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PESs are given in the accompanying EPAPS document.[50] Compilations of level energies $E_J(K,\sigma,v_b)$ for

TABLE IX. Comparisons between calculated and experimental (Refs. 28 and 29) values for the frequencies of spectroscopic mid-IR transitions of the ^{20}Ne–^{12}C^{16}O isotopolog in the subbands involving the first excited bending ($v_b=1$) vibrational level (units: cm^{-1}).

			$\mathrm{XC(fit)}_{r=r_e}$	$\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ plus $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$			SAPT(S)[a]
Subband (v_b,K)=	Branch	No. of lines	RMSD	Δ_{min}	RMSD	Δ_{max}	RMSD
$(1,0) \leftarrow (0,0)$	*P*	4	0.0815	0.0873	0.0920	0.0955	0.0234
	R	2	0.0809	0.0912	0.0926	0.0940	0.0154
$(1,1) \leftarrow (1,0)$	*Q*	12	0.0887	0.0216	0.2147	0.2993	0.8814
$(1,0) \leftarrow (1,1)$	*Q*[b]	12	0.1708	0.0085	0.1035	0.2287	0.8076
$(0,0) \leftarrow (1,0)$	*R*	10	0.0827	0.0231	0.0416	0.0542	0.1086
	P	12	0.1154	0.0119	0.0630	0.1765	0.0805
All above IR lines		52	0.1170	0.0026	0.1052	0.2393	0.5776
All IR lines (Tables VII–IX)		380	0.1480	0.0006	0.1274	0.6779	0.2847

[a] Reference 30.
[b] In Table V of Ref. 29, the label (v_b,K) for the second *Q*-branch column should be read as $(1,0) \leftarrow (1,1)$; see also the text of Sec. 3.2.4 of Ref. 29 (Ref. 71).

$0 \leq J \leq 9$ obtained using the three XC model PESs developed here and for the SAPT(S) PES pair are also given in this document for both the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}(v_{\mathrm{CO}}=0)$ and $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}(v_{\mathrm{CO}}=1)$ complexes for $0 \leq K \leq 3$ and $\sigma = e$, for $1 \leq K \leq 3$ and $\sigma = f$ when $v_b = 0$, and for $(K, \sigma, v_b) = (0, e, 1)$ and $(1, f, 1)$.

V. SUMMARY AND CONCLUSIONS

A set of three 2D Ne–CO PESs having the general form

$$\begin{aligned} V_Y(R,\theta) = 10^{-3} F_Y(\theta) \exp\left\{ \alpha_0 + R \sum_{i=1}^{3} \alpha_i z^{i-1} \right. \\ \left. + \sum_{k=2}^{3} b_k \cos^k \theta \right\} \sum_{\lambda=0}^{6} \sum_{p=0}^{5} a_{\lambda p}(Y) R^p P_\lambda(\cos\theta) \\ - G_{10}(R,\theta) \sum_{n=6}^{10} \sum_{l=0}^{n-4} f_n(R,\theta) C_n^{(l)}(Y) R^{-n} \end{aligned} \tag{9}$$

have been derived in Sec. II. Here, R is the distance between the centers of mass of the Ne atom and the CO molecule and θ is the angle between the CO molecular axis and the line joining the Ne and CO centers of mass, while Y stands for $r = r_e$ and $v_{\mathrm{CO}} = 0$ or $v_{\mathrm{CO}} = 1$ to identify, respectively, the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES for which the CO bond length is fixed at its spectroscopic equilibrium value r_e, the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ vibrationally averaged PES for which the CO molecule is in its ground ($v_{\mathrm{CO}}=0$) vibrational state, or the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ vibrationally averaged PES for which the CO molecule is in its first excited ($v_{\mathrm{CO}}=1$) vibrational state. The $\mathrm{XC(fit)}_{r=r_e}$ PES and the $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=0}$ PES have been obtained from a (stretching-dependent) 3D XC0 PES constructed from first-order Heitler–London Coulomb and exchange energies plus long-range stretching-dependent dispersion and induction energy coefficients through a two-step process: An appropriate replacement of the powers of the CO stretching variable ξ, followed by a refinement of parameters in the multiplicative function $F(\theta)$ and in the components of the long-range composite dispersion and induction energy coefficients to give excellent agreement between theory and experiment for a relatively small set of MMW and/or MW transition frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog. The $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ vibrationally averaged PES was then derived from the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES by replacing the expectation values $\langle \xi^n \rangle_{v_{\mathrm{CO}}=0}$ by $\langle \xi^n \rangle_{v_{\mathrm{CO}}=1}$.

Calculations of the many MW and/or MMW transition frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog that were not employed in the fitting process, as well as of MW and MMW transition frequencies for other Ne–CO isotopologs and of an extensive body of mid-IR data available for both the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ and $^{22}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopologs, have been utilized to test the ability of both the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES and the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ and $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PESs to predict spectroscopic line frequencies. Detailed comparisons of the abilities of the three XC model PESs and of the two SAPT(S) PESs to give accurate MW, MMW, and mid-IR transition frequencies have been presented in Sec. IV.

It is clear from Table IV that both the present rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES and the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES provide levels of agreement with the experimental MW and MMW transition frequencies of Refs. 24–27 for the Ne–CO($v_{\mathrm{CO}}=0$) isotopologs that represent considerable improvements over that available previously. More specifically, the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES gives on the whole significantly better agreement with all 87 observed MW and MMW transition frequencies, as can be seen from the RMSD values of 0.0033 cm^{-1} for the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES versus 0.0094 cm^{-1} for the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES versus 0.0388 cm^{-1} for the SAPT(S) PES for $v_{\mathrm{CO}}=0$. As perhaps can be expected from the methods utilized for their construction, the results obtained from the $\mathrm{XC(fit)}_{r=r_e}$ PES for the MW data alone agrees with experiment by about a factor of 5 better than do those derived from the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES. Both of the XC PESs represent the MW data significantly better than does the SAPT(S) PES.

Although IR transition frequencies for an atom-diatomic molecule dimer can be obtained from the bound energy levels computed from a rigid-rotor PES, the experimental values of the rotational constants for the upper and lower vibrational states of the diatomic molecule and the frequency for the pure vibrational transition in the unperturbed diatomic monomer, this procedure does not reproduce the shift in the molecular vibrational transition frequency caused by the presence of the (perturbing) atom. The present vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ and $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PESs have been constructed not only to alleviate this shortcoming but also to provide more realistic average representations of the stretching dependence of the interaction between Ne atoms and CO molecules in specific vibrational states. Employment of the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair for the calculation of the mid-IR transition frequencies for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog gives a redshift of 0.077 cm^{-1} for the mid-IR spectral lines that is in excellent agreement with experiment (0.072 cm^{-1}), comparable in reliability to the result obtained from the SAPT(S) PES pair, and a marked improvement over the result (0.012 cm^{-1}) obtained from the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES.

The RMSD values shown in Table IX for the calculations employing the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair, the $\mathrm{XC(fit)}_{r=r_e}$ PES, and the SAPT(S) PES pair for 380 experimentally observed mid-IR lines are 0.127, 0.148, and 0.285, respectively; overall, for the mid-IR transitions, the vibrationally averaged XC PES pair and the $\mathrm{XC(fit)}_{r=r_e}$ PES both offer an improvement of about a factor of 2 relative to the spectral results obtained from the SAPT(S) PES pair. While the agreement with experiment is clearly superior for the XC PES pair for the $K=0$ and 1 subbands of the mid-IR spectra not involving $v_b=1$ states (see Tables VII and VIII) this is not so clearly the case for the $K=2$ ad 3 subbands for the $^{20}\mathrm{Ne}-{}^{12}\mathrm{C}^{16}\mathrm{O}$ isotopolog or for the combination bands (Table IX) where the $\mathrm{XC(fit)}_{r=r_e}$ results are comparable to those obtained for the vibrationally averaged XC PES pair.

When 467 (specifically, all 30 MW plus all 57 MMW plus 380 mid-IR) of the 528 available spectroscopic transitions are considered, the corresponding RMSD values for the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair, the $\mathrm{XC(fit)}_{r=r_e}$ PES, and the SAPT(S) PES pair are 0.114, 0.133, and 0.226, from which it can be seen that the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}/\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PES pair gives systematically better agreement with the observed spectroscopic data than does the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES or the scaled *ab initio* SAPT(S) PES pair. Even though the improvement, relative to the rigid-rotor $\mathrm{XC(fit)}_{r=r_e}$ PES, in the level of agreement between calculated and experimental spectral frequencies obtained using the vibrationally averaged XC PES pair appears to be relatively small for Ne–CO dimers when all spectral frequencies are considered, it is likely to become much more important and significant for systems such as Ar–CO, Kr–CO, and Xe–CO, for which the observed shifts of the fundamental CO vibrational frequency are much larger, namely, $-0.440\ \mathrm{cm}^{-1}$ for Ar–CO,[66] $-0.630\ \mathrm{cm}^{-1}$ for Kr–CO,[67] and $-0.867\ \mathrm{cm}^{-1}$ for Xe–CO.[68] Of course, as illustrated above for particular subsets of spectral frequencies, the improvement in representing the experimental results are markedly better for the XC PES pair or for the $\mathrm{XC(fit)}_{r=r_e}$ PES relative to the SAPT(S) PES pair.

Applications of rigid-rotor or vibrationally averaged PESs in representing the interaction of Ne with a CO molecule have been emphasized here. The starting point, the initial 3D XC(0) PES developed in Sec. II A, has an explicit representation of the CO bond stretching that can be utilized to develop more reliable explicit 3D PESs for the Ne–CO interaction. For example, a probable improvement on the 3D XC(0) PES for the $\mathrm{Ne-CO}(v_{\mathrm{CO}}=0)$ interaction can be obtained from the 2D $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES simply by replacing the parameter $a_{\lambda p}(v_{\mathrm{CO}}=0)$ by $\Sigma_{n=0}^{2} a_{\lambda p}^{(n)} \xi^n$ and the vibrationally averaged long-range energy coefficients $C_n^{(l)}(\mathrm{fit}, v_{\mathrm{CO}}=0) = Q_n^{(l)}(v_{\mathrm{CO}}=0)\Sigma_{k=0}^{3} C_{nk}^{(l)} \langle \xi^k \rangle_{v_{\mathrm{CO}}=0}$ by $C_{nk}^{(l)}(v_{\mathrm{CO}}=0, \xi) = Q_n^{(l)}(v_{\mathrm{CO}}=0)\Sigma_{k=0}^{3} C_{nk}^{(l)} \xi^k$, with the CO bond stretching of each composite long-range interaction energy coefficient normalized so that the corresponding fit coefficient is reproduced upon vibrational averaging. Additional flexibility can be introduced by allowing each k-vibrational component $C_{nk}^{(l)}$ of $C_n^{(l)}(v_{\mathrm{CO}}=0, \xi)$ to vary within its estimated uncertainty and by introducing a bond-stretching dependence into the function F multiplying the Heitler–London energy when fitting to experimental constraints. Examples of this approach are provided by the development of 3D PESs for the $\mathrm{H_2-Ar}$ interaction by Bissonnette *et al.*[7] and for the $\mathrm{H_2-Kr}$ interaction by Wei *et al.*;[8] in both cases, the parameters in the XC PESs were obtained by fitting to selected IR spectroscopic data. The 3D XC(0) PES for Ne–CO and its modifications discussed briefly here add to the family[43,69,70] currently available for noble gas–CO dimers. It is worth emphasizing here that the relatively small differences between a 2D rigid-rotor PES, such as the $\mathrm{XC(fit)}_{r=r_e}$ PES, and the vibrationally averaged $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ and $\overline{\mathrm{XC}}_{v_{\mathrm{CO}}=1}$ PESs are important both in principle and in practice, especially for mid-IR spectroscopic transitions.

In a subsequent publication[64] it will be shown that both the $\mathrm{XC(fit)}_{r=r_e}$ PES and the $\overline{\mathrm{XC(fit)}}_{v_{\mathrm{CO}}=0}$ PES determined in the present study also give results for all known Ne–CO beam scattering cross sections and bulk properties of Ne–CO mixtures that agree well with experiment. Taken together with the present results for the MW, MMW, and mid-IR spectral transitions of the Ne–CO dimer, these results make it apparent that these XC model PESs provide the best available representation of the Ne–CO interaction.

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