Potential Energy Landscape of CO Adsorbates on NaCl(100) and Implications in Isomerization of Vibrationally Excited CO

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ABSTRACT: Several full-dimensional potential energy surfaces (PESs) are reported for vibrating CO adsorbates at two coverages on a rigid NaCl(100) surface based on first-principles calculations. These PESs reveal a rather flat energy landscape for physisorption of vibrationless CO on NaCl(100), evidenced by various C-down adsorption patterns within a small energy range. Agreement with available experimental results is satisfactory, although quantitative differences exist. These PESs are used to explore isomerization pathways between the C-down and higher-energy O-down configurations, which reveal a significant isomerization barrier. As the CO vibration is excited, however, the energy order of the two isomer changes, which helps to explain the experimental observed flipping of vibrationally excited CO adsorbates.

I. INTRODUCTION

CO adsorption on surfaces of salt crystals such as NaCl has provided an ideal proving ground to study vibrational energy flow among weakly interacting molecules with well-defined separation and orientation.1 The interaction between the CO adsorbate and the ionic surface is dominated by weak electrostatic (ES) and van der Waals (vdW) interactions, as evidenced by a relatively low adsorption energy and a small CO frequency shift.2,3 For CO in its ground vibrational state,4 adsorption at the Na+ site,4 thanks to the slightly negative charge in carbon. The adsorbate–substrate interaction is weak but long-range interadsorbate interactions. The energy landscape of the CO adsorption is thus quite flat near the equilibrium adsorption geometry.5–9 At high temperatures, the CO monolayer (ML) on NaCl(100) has a two-dimensional 1 × 1 lattice with CO oriented perpendicular to the surface, while this structure transforms to a 2 × 1 lattice with tilted CO at temperatures lower than 35 K.10–12

In a series of pioneering papers about 30 years ago, Chang and Ewing demonstrated that laser excitation of CO molecules adsorbed on cold NaCl(100) surfaces to their low-lying vibrational states (ν = 1) can lead to facile energy transfer among the adsorbates, resulting in some highly excited CO molecules, which can be detected from their spontaneous emission.13–15 This so-called vibrational energy pooling has since attracted much attention from both theoretical16–18 and experimental fronts.19 Very recently, high-resolution spectra of the CO on the cold NaCl(100) system have been measured suggesting that the energy pooling can result in a population of CO vibrational states as high as ν = 30.20,21 More interestingly, these highly vibrationally excited CO species are observed to flip from a C-down geometry to an O-down geometry, thus providing an interesting example of double-well systems coupled to a condensed medium.21 To better understand the energy resonant energy transfer between two vibrationally excited CO adsorbates is very efficient, even when they are separated by a few lattice sites, and the small energy release can be soaked up by phonons of the cold surface.20 This vibrational exchange process dominates over direct CO vibrational relaxation (CO(ν) → CO(ν − 1)), which requires many phonons to accept the large energy release associated with the loss of a vibrational quantum, as the Debye frequency of the NaCl surface is merely 223 cm−1. The reverse endoergic ladder-descending process is essentially dampened on cold surfaces by the Boltzmann factor, and thus negligible at low temperatures. Interestingly, such vibrational energy exchange is also operative in the gas phase,23–25 for applications such as a supersonic CO laser.26 The ladder climbing is realized in the gas environment by collisions, by the same principle as mentioned above.

Very recently, high-resolution spectra of the CO on the cold NaCl(100) system have been measured suggesting that the energy pooling can result in a population of CO vibrational states as high as ν = 30.20,21 More interestingly, these highly vibrationally excited CO species are observed to flip from a C-down geometry to an O-down geometry, thus providing an interesting example of double-well systems coupled to a condensed medium.21 To better understand the energy transfer, the potential energy landscapes (PESs) must be considered.
pooling and the resulting isomerization processes, one needs to map out the global potential energy surface (PES) for CO adsorption on NaCl with the C–O vibrational coordinate included, which is the main objective of this work. To this end, we report several global PESs for CO adsorption on a rigid NaCl(100) surface based on analytical representations of density functional theory (DFT) points using a machine learning method. Several different functionals were tested, and two vDW-corrected ones were used in generating the DFT points. We emphasize that these PESs differ from previous empirical ones in that the interaction is computed using experimental lattice constant of 5.640 Å with D3(BJ), and 5.664 Å with PBE-MBD@rsSCS/FI. The lattice constant of 5.697 Å with PBE, 5.583 Å with PBE-ML coverage, respectively. The optimized NaCl lattice has a description by projector-augmented wave (PAW) potentials. In order to systematically focus on the D3(BJ) and the two vDW-corrected DFT methods, the D3 method with Becke–Johnson damping (PBE-D3(BJ)), and the revised many-body dispersion energy method including fractionally ionic contributions to the polarizability (PBE-MBD@rsSCS/FI), were employed.

The NaCl(100) surface was modeled by a two-layer slab, and the CO overlayer is simulated in p(1 × 1) (and p(2 × 1)) or p(2 × 2) surface unit cells, corresponding to 1 ML or 1/4 ML coverage, respectively. The optimized NaCl lattice has a lattice constant of 5.697 Å with PBE, 5.583 Å with PBE-D3(BJ), and 5.664 Å with PBE-MBD@rsSCS/FI. The experimental lattice constant of 5.640 Å differs by less than 0.06 Å from these theoretical values. In order to systematically focus on the differences of the exchange-correlation functional in this study, we have thus used the experimental values for the rigid NaCl slab in all our calculations. The vacuum space between the periodic slabs in the Z-direction was set to 15 Å. The interaction between ionic cores and electrons was described by projector-augmented wave (PAW) potentials. A Monkhorst–Pack k-points grid was used, and the plane wave expansion was truncated at a kinetic energy of 700 eV. The convergence properties of slab layers and k-points are provided in Figure S1 in Supporting Information (SI).

II.B. Data Sampling and PES Fitting. Since the full-dimensional PES is designed to cover the entire configuration space, it requires points near the adsorption equilibrium as well as the desorption asymptote for vibrationally excited CO. The data sampling was started by extracting the geometries and energies from ab initio molecular dynamics (AIMD) trajectories of CO on the NaCl(100) surface. These trajectories were launched at 6.0 Å from the surface with CO(νc = 0–40), directed toward the surface along the surface normal. The CO molecule is randomly oriented, but with zero rotational angular momentum. A geometric criterion of 0.1 Å based on the root-mean-square deviation (RMSD) of the Euclidean distance between two points was applied to exclude points that were too close to each other. A primitive PES was constructed on the basis of the first batch of approximately 3000 geometries. Additional points were sampled by running quasiclassical trajectory (QCT) calculations with various initial conditions (νc = 0–40) on this primitive PES. A new point was included into the data set if it satisfied the aforementioned geometric criterion and an additional energetic criterion given by RMSD of energies predicted by five different fits of the data. Specifically, the energetic criterion excludes those points with almost the same predicted results from different fits, as the fit can be considered to be converged at these locations. Then, the PES was updated using the new data set. This procedure was repeated iteratively, and the PES was considered to be fully converged if no point below 2.5 eV can be found from a new batch of trajectories, with the energetic criterion set to 10 cm−1. This systematic data sampling approach has been validated in various gas-phase and molecule–surface interaction systems. Finally, 16 196 symmetry unique points were sampled.

Feed forward neural networks (NNs) with two hidden layers were employed to fit the six-dimensional PESs. All the 16 196 points were projected to the irreducible triangle of the NaCl(100) surface unit cell in advance, as shown in Figure 1a,b. Any points outside this symmetry unique region can be obtained by the symmetry of the surface. To ensure the

Figure 1. Spatial and energy distributions of all the configurations used for PES construction and the definition of the coordinates used to describe the geometries: (a) distribution on the p(1 × 1) unit cell, (b) distribution on the p(2 × 2) unit cell, (c) spatial distribution on the height of the CO molecule to the surface and rCO, (d) potential energy (2 × 2-MBD) as a function of rCO, and (e, f) definition of the coordinates in top (e) and side (f) views. The Na+ and Cl− are represented by blue and yellow circles, respectively.
Table 1. Adsorption Energies, Geometries, and CO Frequencies for Minima Optimized in the \( p(1 \times 1) \) Surface Unit Cell (1 ML) Using Different Functionals*  

| method          | geometry | adsorption energy (cm\(^{-1}\)) | \( v_{CO} \) (cm\(^{-1}\)) | \( r_{CO} \) (Å) | \( dz^2 \) (Å) | tilt (deg) | azimuthal (deg) | \( dy^2 \) (Å) | \( dx^2 \) (Å) |
|-----------------|----------|---------------------------------|-----------------------------|------------------|--------------|-------------|----------------|--------------|--------------|
| PBE C-down s1   | −885.39  | 2132.58                         | 1.1352                      | 3.1581           | 30.19       | 1.96        | 0.0447         | 0.6588       |
| C-down s2       | −883.77  | 2138.32                         | 1.1355                      | 3.1946           | 27.37       | 45.00       | 0.4270         | 0.4270       |
| C-down s3       | −818.79  | 2136.91                         | 1.1349                      | 3.2826           | 2.93        | 44.56       | 0.0405         | 0.0399       |
| O-down s4       | −352.24  | 2125.32                         | 1.1360                      | 3.3512           | 143.39      | −135.04     | 0.1930         | 0.2114       |
| O-down s5       | −312.04  | 2135.64                         | 1.1358                      | 3.3468           | 180         | 0           | 0              | 0            |
| PBE-D3(BJ) C-down s1 | −1996.07 | 2139.18                         | 1.1353                      | 3.0412           | 36.13       | 3.77        | 0.0557         | 0.8328       |
| C-down s1       | −1974.58 | 2137.44                         | 1.1351                      | 3.1061           | 32.16       | 45.00       | 0.5200         | 0.5200       |
| C-down s2       | −1977.76 | 2132.72                         | 1.1352                      | 3.1068           | 33.72       | 39.34       | 0.5033         | 0.5886       |
| O-down s4       | −1433.25 | 2125.80                         | 1.1365                      | 3.0558           | 122.78      | −135.15     | 0.2696         | 0.2656       |
| O-down s5       | −1409.89 | 2134.05                         | 1.1348                      | 3.1128           | 31.00       | 3.28        | 0.0495         | 0.6472       |
| PBE-MBD@rsSCS/FI C-down s1 | −1501.79 | 2135.55                         | 1.1348                      | 3.1128           | 31.00       | 3.28        | 0.0495         | 0.6472       |
| C-down s2       | −1490.89 | 2134.05                         | 1.1348                      | 3.1439           | 27.95       | 45.00       | 0.4189         | 0.4189       |
| C-down s3       | −1416.46 | 2150.18                         | 1.1345                      | 3.2505           | 7.61        | 45.00       | 0.0617         | 0.0614       |
| O-down s4       | −909.44  | 2122.67                         | 1.1360                      | 3.1982           | 141.37      | −136.60     | 0.1779         | 0.2026       |

*The global minimum in each case is given in bold. The harmonic frequencies for free CO are 2131.8, 2134.3, and 2130.5 cm\(^{-1}\) for the three functionals, respectively.  
| a | The height of CO to surface \( dz \) is defined as \((dZ_C + dZ_O)/2\).  
| b | The lateral displacements \( dx/dy \) correspond to \( dX_C/dY_C \) for C-down configurations, and \( dX_O/dY_O \) for O-down configurations.

Figure 2. Illustration of geometries C-down s1/2/3 and O-down s4 optimized by the PBE functional in the \( p(1 \times 1) \) and \( p(2 \times 2) \) unit cells. The Na\(^+\), Cl\(^-\), O, and C are represented by blue, yellow, red, and gray circles, respectively.
Table 2. Adsorption Energies, Geometries, and CO Frequencies for Minima Optimized in the $p (2 \times 1)$ Surface Unit Cell (1 ML) Using Different Functionals

| method          | geometry | adsorption energy (cm$^{-1}$) | $r_{CO}$ (cm$^{-1}$) | $r_{CO}$ (Å) | $dZ^b$ (Å) | tilt (deg) | azimuthal (deg) | $dX^c$ (Å) | $dY^c$ (Å) |
|-----------------|----------|-------------------------------|----------------------|--------------|------------|------------|----------------|------------|------------|
| PBE             | C-down s1 | $-891.30$                      | 2121.8/2124.2        | 1.1350       | 3.1391     | 31.83      | $65.66$        | 0.7163     | 0.0487     |
|                 | C-down s2 | $-884.92$                      | 2135.0/2128.8        | 1.1355       | 3.2133     | 25.67      | $49.92$        | 0.4044     | 0.3757     |
|                 | C-down s3 | $-902.70$                      | 2131.1/2123.9        | 1.1351       | 3.1375     | 33.48      | $\pm 89.42$    | $\pm 0.7633$| 0.0152     |
|                 | C-down s4 | $-889.98$                      | 2134.1/2128.0        | 1.1354       | 3.2085     | 25.66      | $\pm 47.30$    | $\pm 0.4116$| 0.3765     |
|                 | C-down s5 | $-892.58$                      | 2136.3/2131.7        | 1.1352       | 3.1918     | 27.27      | $\pm 21.21$    | $\pm 0.2217$| 0.5467     |
|                 | O-down s6 | $-352.99$                      | 2127.0/2126.7        | 1.1357       | 3.3078     | 142.13     | $-146.76$      | 0.1252     | 0.3191     |
|                 | O-down s7 | $-352.67$                      | 2121.0/2123.1        | 1.1357       | 3.2222     | 144.01     | $\pm 153.07$   | 0.0152     | 0.3031     |
| PBE-D3(BJ)      | C-down s1 | $-2004.20$                     | 2128.2/2130.8        | 1.1353       | 3.0454     | 35.83      | 87.11          | 0.8152     | 0.0327     |
|                 | C-down s2 | $-1988.55$                     | 2139.6/2134.6        | 1.1363       | 3.0418     | 35.83      | 48.65          | 0.6134     | 0.5631     |
|                 | C-down s3 | $-2008.54$                     | 2134.3/2126.8        | 1.1354       | 3.0462     | 35.42      | $\pm 87.08$    | $\pm 0.8032$| 0.0431     |
|                 | C-down s4 | $-1987.13$                     | 2134.5/2129.2        | 1.1342       | 3.1060     | 31.38      | $\pm 44.40$    | $\pm 0.5177$| 0.5121     |
|                 | C-down s5 | $-1999.73$                     | 2133.9/2131.3        | 1.1345       | 3.0905     | 31.47      | $\pm 30.83$    | $\pm 0.2281$| 0.6940     |
|                 | O-down s6 | $-1406.80$                     | 2130.5/2129.5        | 1.1358       | 3.1583     | 137.93     | $-146.76$      | 0.0933     | 0.2440     |
|                 | O-down s7 | $-1403.73$                     | 2127.2/2125.2        | 1.1366       | 3.1415     | 134.51     | $\pm 153.71$   | $\pm 0.0885$| 0.3972     |
| PBE-MBD@rsSCS/FI | C-down s1 | $-1542.17$                     | 2138.6/2130.9        | 1.1349       | 3.0590     | 33.83      | 87.03          | 0.7665     | 0.0215     |
|                 | C-down s2 | $-1531.22$                     | 2134.8/2128.7        | 1.1354       | 3.1240     | 28.33      | 46.02          | 0.4451     | 0.4363     |
|                 | C-down s3 | $-1549.95$                     | 2133.8/2126.3        | 1.1353       | 3.0558     | 34.43      | $\pm 87.51$    | $\pm 0.7737$| 0.0279     |
|                 | C-down s4 | $-1523.92$                     | 2137.4/2131.1        | 1.1340       | 3.1467     | 26.16      | $\pm 46.94$    | $\pm 0.3932$| 0.3781     |
|                 | C-down s5 | $-1534.89$                     | 2137.3/2133.2        | 1.1353       | 3.1112     | 29.65      | $\pm 17.40$    | $\pm 0.2022$| 0.6070     |
|                 | O-down s6 | $-942.587$                     | 2129.9/2129.2        | 1.1359       | 3.1459     | 140.58     | $-148.24$      | 0.1204     | 0.2967     |
|                 | O-down s7 | $-943.903$                     | 2130.2/2129.6        | 1.1360       | 3.1463     | 140.50     | $\pm 149.19$   | $\pm 0.1292$| 0.2895     |

The global minimum in each case is given in bold. The harmonic frequencies for free CO are 2131.8, 2134.3, and 2130.5 cm$^{-1}$ for the three functionals, respectively. The experimental structure information is included for comparison.

$b$ The height of CO to surface $dZ$ is defined as ($dZ_C + dZ_O) / 2$.
$c$ The lateral displacements $dX/dY$ correspond to $dX_C/dY_C$ for C-down configurations, and $dX_O/dY_O$ for O-down configurations.

Figure 3. Illustration of geometries C-down s1−s5 and O-down s6/7 in the $p (2 \times 1)$ unit cell. Results from different functionals are similar. The Na+, Cl−, O, and C are represented by blue, yellow, red, and gray circles, respectively.
Table 3. Adsorption Energies, Geometries, and CO Frequencies for Minima Optimized in the p(2 × 2) Surface Unit Cell (1/4 ML) Using Different Functionals

| method        | geometry | adorption energy (cm⁻¹) | v_CO (cm⁻¹) | r_CO (Å) | d_Z(Å) | tilt (deg) | azimuthal (deg) | d_Y(Å) | d_X(Å) |
|---------------|----------|-------------------------|-------------|----------|--------|-----------|---------------|--------|--------|
| PBE           | C-down s1| −887.08                | 2131.46     | 1.1349   | 3.1353 | 30.34     | 2.12           | 0.0341 | 0.7164 |
|               | C-down s2| −900.15                | 2136.19     | 1.1346   | 3.1822 | 23.78     | 45.00          | 0.3983 | 0.3983 |
|               | C-down s3| −912.44                | 2138.73     | 1.1342   | 3.3207 | 0.60      | 0              | 0.0010 | 0      |
|               | O-down s4| −351.43                | 2124.66     | 1.1357   | 3.2118 | 169.74    | −135.00        | 0.0822 | 0.0822 |
|               | O-down s5| −367.30                | 2131.33     | 1.1360   | 3.3351 | 180       | 0              | 0      | 0      |
| PBE-D3(BJ)    | C-down s1| −1767.55               | 2140.76     | 1.1344   | 3.0671 | 31.16     | 1.68           | 0.0415 | 0.7267 |
|               | C-down s2| −1748.42               | 2141.84     | 1.1344   | 3.0846 | 27.95     | 45.00          | 0.4963 | 0.4963 |
|               | C-down s3| −1715.79               | 2145.05     | 1.1338   | 3.2459 | 0.01      | 0              | 0.0001 | 0      |
|               | O-down s4| −1102.07               | 2128.97     | 1.1354   | 3.1813 | 169.72    | −135.00        | 0.0846 | 0.0846 |
| PBE-MBD@rsSCS/FI | C-down s1| −1381.28               | 2134.27     | 1.1341   | 3.2019 | 17.66     | 0              | 0      | 0.3900 |
|               | C-down s2| −1376.63               | 2138.23     | 1.1343   | 3.1559 | 23.56     | −135.00        | 0.3950 | 0.3950 |
|               | C-down s3|                     |             |          |        |           |                |        |        |
|               | O-down s4|                     |             |          |        |           |                |        |        |
|               | O-down s5| −784.67                | 2123.37     | 1.1357   | 3.2448 | 180       | 0              | 0      | 0      |
|               | C-down s6| −1379.56               | 2147.67     | 1.1339   | 3.2466 | 0         | 0              | 0      | 0      |

“The global minimum in each case is given in bold. The harmonic frequencies for free CO are 2131.8, 2134.3, and 2130.5 cm⁻¹ for the three functionals, respectively. The height of CO to surface dZ is defined as (dZ_C + dZ_O)/2. The lateral displacements dX/dY correspond to dX_C/dY_C for C-down configurations, and dX_O/dY_O for O-down configurations.”

The local and global potential minima for the p(1 × 1) surface unit cell (1 ML) were optimized using different DFT methods, and the corresponding energies, geometries, and CO vibrational frequencies are listed in Table 1. The coordinates used to describe these geometries are depicted in Figure 1e,f. In addition to three tilted C-down minimum energy structures, a tilted O-down minimum has been located at a significantly higher energy. They are denoted as s1, s2, s3, s4 hereafter, and their images are shown in Figure 2. For the results using the PBE functional, the global minimum corresponds to the s1 geometry, which has a tilt angle of 30.19°, a very small azimuthal angle of 1.96°, and a significant lateral displacement of the carbon atom, dx_C = 0.654 Å and dy_C = 0.0447 Å, from the top Na⁺ site. This configuration features a CO molecule shifted from one surface Na⁺ site to a neighboring Na⁺ site, as illustrated in Figure 2. In contrast, the other two C-down minima have azimuthal angles nearly 45°, shifted from the Na⁺ site to the neighboring Cl⁻ site. The tilt angle of s2 is somewhat smaller than that of s1, while the s3 is very close to the perpendicular configuration. The O-down minimum s4 has a tilt angle of 143.39° (=138°−36.61°), and also large shifts in both X- and Y-directions; this resembles the C-down s2 configuration. In addition, there exists a perpendicular O-down minimum, denoted as s5, but only with the PBE functional. These adsorption configurations are qualitatively the same for the two vdW-corrected functionals, PBE-D3(BJ) and PBE-MBD@rsSCS/FI, although the C-down s3 configuration from PBE-D3(BJ) is more tilted and shifted from the Na⁺ site.

We have also investigated the CO structure in the p(2 × 1) unit cell, which is known to exist on NaCl(100) at temperatures below 35 K.10,11 Like the p(1 × 1) model described above, this model corresponds to 1 ML coverage, but it allows two CO in the surface unit cell to orient differently. Optimization results show that the two CO species in a unit cell have exactly the same values of r_CO, dZ, and tilt angles, and the only difference is the sign of the azimuthal angle. As shown in Table 2 and Figure 3, seven minimum energy structures, five C-down and two O-down, have been found. Among them, the C-down s1 and s2 structures are identical to those in the p(1 × 1) (1 ML) model. The relaxation of the relative orientation of the two CO molecules in the unit cell allows additional adsorption patterns, leading to two minimum energy structures that were first discussed in the work of Vogt and Vogt.12 The antiparallel minimum C-down s3 is the global minimum in the p(2 × 1) model with all three functionals, which can be generated from s1 with opposite azimuthal angles and lateral displacements of dY for the two CO molecules on the neighboring Na⁺ sites. On the other hand, the herringbone minimum s4 has close absolute values of geometry parameters with s2 but different signs in the azimuthal angle and a slightly different dZ value. Another minimum, denoted as s5, which is similar to s4 but has smaller azimuthal angles, has also been located. In a comparison with s2, s4 has a slightly higher energy, and s5 is energetically more favorable. In addition, a herringbone O-down minimum s7 has been located in the p(2 × 1) model, which has an almost undistinguishable adsorption energy from that of the minimum s6. The energetic similarities between s1/s3 and between s2/s4/s5 in the p(2 × 1) model indicate that the p(1 × 1) model should be good enough for describing the energy landscape of the CO adsorbate on NaCl(100), apart from the orientational differences.”
The C-down minima found in the $p(2 \times 1)$ (1 ML) model were also reported by Boese and Saalfrank. These authors also found other tilted configurations with irregular or spiral oriented CO (denoted as T/I or T/S, respectively) in larger unit cells. For each size of the unit cell, the antiparallel configuration remains to be the most energetically favorable. Interestingly, the C-down minima obtained from the $p(1 \times 1)$ and $p(2 \times 1)$ models can be identified in the local structures of T/I or T/S configurations. The combination of these minima in Tables 1 and 2, which have similar energies, results in the richness and diversity of configurations in larger unit cells.

The geometry of the calculated global minimum (anti-parallel, $s3$) can be compared with experimental geometric information obtained from LEED, which is also listed in Table 2. Both the CO bond length and the height ($dZ$) are in good agreement with the experimental estimation. However, its tilt angle is larger than the experimental value. In fact, the experimental tilt and azimuthal angles are closer to the herringbone structure ($s4$), which has a slightly higher energy. As discussed below, the energy landscape is quite flat, and these two structures ($s3$ and $s4$) might be sufficiently close in energy to interconvert, even at low temperatures. Thus, we conclude that the overall agreement with the experiment is satisfactory, albeit with some quantitative uncertainties. A likely source of the uncertainties is the inaccuracy of the DFT functional, which might be responsible for the noticeable differences in Table 2. More accurate electronic structure methods, such as those based on correlated wave functions, are need to provide a quantitative comparison for this floppy system. Another promising approach is to express the interactions in a pairwise form in which the interactions are obtained with a high-level ab initio method. In addition, some of the uncertainties may also derive from the finite experimental temperature (25 K), which might require a free-energy simulation to make the direct comparison with experiment, due to the floppy nature of the system. Furthermore, as already suggested by Vogt and Vogt, it might be necessary to reanalyze the LEED data by including anisotropic thermal displacements which our calculations can provide. We are currently investigating whether this can improve the agreement with the experiment.

For the $p(2 \times 2)$ surface unit cell, corresponding to a lower CO coverage of 1/4 ML, the local and global minima have also been determined, and their information is listed in Table 3. Their images are given in Figure 2. Interestingly, the tilt angles and lateral shifts from two vdW-corrected functionals are all smaller compared to the corresponding geometries from Tables 1 and 2, presumably due to the larger CO–CO distances and hence weaker CO–CO interactions. With the PBE functional, the global minimum, the C-down $s3$, has a very small tilt angle (0.6°) and almost no lateral shift, located at the top site of the Na+ site. In contrast, results obtained with both the PBE-D3(BJ) and PBE-MBD@rsSCS/FI functionals predict the C-down $s1$ configuration as the global minimum, similar to that of the $p(1 \times 1)$ model. No tilted O-down minimum was found using the PBE-MBD@rsSCS/FI functional.

From Tables 1–3, it is clear that all C-down minima in all three scenarios have very similar energies, suggesting a relatively flat potential landscape. These are all typically physisorption, judging from the small shifts in bond length and frequency from the free CO. Figure 4 plots the adsorption potential energy curves (PECs) as a function of distance from the C atom of CO to the NaCl surface, calculated with different methods for the $p(1 \times 1)$ (1 ML) and $p(2 \times 2)$ (1/4 ML) models. The minima of these PECs correspond to the global minimum C-down configurations shown in Tables 1 and 3.

The energy zero is defined as the sum of the energy of the clean surface and the energy of a single free CO molecule placed in a large box (20 × 20 × 20 Å$^3$). The adsorption energies in the $p(1 \times 1)$ (1 ML) model are generally larger than those in the $p(2 \times 2)$ (1/4 ML) model, due to the attractive CO–CO interactions. For the same reason, the potential energies in the $p(1 \times 1)$ (1 ML) model do not vanish when the CO molecule desorbs, except for the PEC from the PBE functional, which lacks vdW interactions between CO molecules. In a comparison with the adsorption energy (−1504 cm$^{-1}$ or −18.0 kJ/mol) obtained from the experiments by Richardson et al., the PBE functional grossly underestimates due apparently to the lack of the vdW interaction, but the PBE-D3(BJ) functional substantially overestimates. On the other hand, the PBE-MBD@rsSCS/FI functional is in good agreement with experiment and the high-level QM-QM embedding result of −17.8 kJ/mol by Boese and Saalfrank, presumably because of a balanced description of the vdW corrections. We note in passing that all of the functionals considered here yield zero-point energy corrections that destabilize the adsorption energies by about +2.4 kJ/mol for the $p(1 \times 1)$ and $p(2 \times 1)$ structures, which is in qualitative but not quantitative agreement with the estimate of 4–5 kJ/mol by Richardson et al. Finally, the equilibrium adsorption height, which is defined as the distance between C and the surface, is measured to be 2.59 Å, which is reproduced with reasonable accuracy by all three methods, as shown in the figure.

### III.B. Potential Energy Surfaces

Because of the poor performance of the PBE functional in reproducing the adsorption energy, it is not considered in future discussions. Instead, both vdW-corrected functionals, PBE-D3(BJ) and PBE-MBD@rsSCS/FI, are used for the construction of the six-dimensional PESs, describing the adsorption of one CO molecule in the $p(1 \times 1)$ and $p(2 \times 2)$ surface unit cells, respectively. The 12-dimensional PES for $p(2 \times 1)$ was not attempted, because the potential landscape is qualitatively similar to that of $p(1 \times 1)$, as discussed above. The 16 196 configurations used for PES fitting are distributed evenly on the irreducible zone of the NaCl(100) surface, as shown in Figure 1a for the $p(1 \times 1)$ model and Figure 1b for the $p(2 \times 2)$ model.
2) model. Distribution of the data points in the height of the CO molecule to the surface, the bond length of CO, as well as the total potential energy are illustrated in Figure 1c,d. Four PESs have been constructed, denoted hereafter as (a) $2 \times 2$-MBD, (b) $2 \times 2$-D3, (c) $1 \times 1$-MBD, and (d) $1 \times 1$-D3, with the fitting RMSE values of 3.68, 3.60, 5.71, and 5.68 meV, respectively. The distribution of fitting errors is displayed in Figure S2 as a function of potential energy, in which the four PESs perform similarly. The PESs can be obtained from the corresponding author upon request.

Figure 5 shows the contour plots of the PESs as a function of the tilt angle and height of CO (defined as $dZ = (dZ_C + dZ_O)$) for $2 \times 2$-MBD and $1 \times 1$-MBD PESs. The red markers “A” to “D” are the global C-down and O-down minima. The interval of the contours is 100 cm$^{-1}$.

Figure 5. Contours of PES as a function of the tilt angle and the height of the CO molecule to the surface, with $r_{CO}$ fixed at equilibrium (1.132 Å), and the other three coordinates optimized. Panels a–d correspond to $2 \times 2$-MBD, $2 \times 2$-D3, $1 \times 1$-MBD, and $1 \times 1$-D3 PESs, respectively. The red markers “A” to “D” are the global C-down and O-down minima. The interval of the contours is 100 cm$^{-1}$.

As shown in Tables 1 and 3, the PESs are relatively flat with several C-down minima within a small energy range. Figure 6 shows the PES of the CO adsorbate on different adsorption sites, with the C–O bond fixed at its equilibrium and three other coordinates ($dZ_C$, the tilt and azimuthal angles) optimized. Due to the similarity between PBE-MBD@rsSCS/FI and PBE-D3(BJ) functionals, only the results on $2 \times 2$-MBD and $1 \times 1$-MBD PESs are displayed. The C-down $s1/s2/s6$ structures on the $2 \times 2$-MBD PES, and $s1/s2/s3$ structures on the $1 \times 1$-MBD PES, can be clearly observed. For the $2 \times 2$-MBD PES, the $s1/s2$ and $s6$ configurations have similar energies, with differences smaller than 5 cm$^{-1}$ between each other. As a result, the PES is very flat on top and around the Na$^+$ site. In contrast, on the $1 \times 1$-MBD PES, the C-down $s1/s2$ configurations have potential energies almost 80 cm$^{-1}$ lower than $s3$, thus, the adsorbed CO molecules are generally shifted from the Na$^+$ site.

To shed light on the energy landscape for a vibrationally excited CO adsorbate on NaCl(100), Figure 7 shows the PESs between a stretched CO molecule with the NaCl(100) surface, with the bond length $r_{CO}$ fixed at 1.596 Å and the other three dimensions optimized. The $r_{CO}$ corresponds to the outer turning point of CO($v = 20$). The red markers “E” to “H” correspond to the global and local “minima”. The interval of the contours is 100 cm$^{-1}$.

Figure 6. Contours of the PES for CO diffusion among different sites, with $r_{CO}$ fixed at the equilibrium (1.132 Å), and the other three coordinates optimized: (a) $2 \times 2$-MBD PES and (b) the $1 \times 1$-MBD PES. The red markers “s1” to “s3” correspond to the tilted C-down minima defined in Figure 5. The interval of the contours is 5 cm$^{-1}$.

Figure 7. Same as Figure 5, but with $r_{CO}$ fixed at 1.596 Å which is the outer turning point of CO($v = 20$). The red markers “E” to “H” correspond to the global and local “minima”. The interval of the contours is 100 cm$^{-1}$.
C\textsuperscript{6+} atom adsorbed to the surface Cl\textsuperscript{−} atom, as illustrated in Figure 3. The higher minima, as marked by “E” and “G” in Figure 7b,c, also have an adsorption geometry nearly parallel to the surface plane with the O\textsuperscript{6+} atom adsorbed to the surface Na\textsuperscript{+} site, and the C\textsuperscript{6+} atom toward the middle point of two adjacent Cl\textsuperscript{−} sites. The “F” minimum on the 2 × 2-MBD PES is −4094.4 cm\textsuperscript{−1}. The landscape for the 1 × 1-MBD and 1 × 1-D3 PESs is similar, as shown in Figure 7c,d, except the barrier between the wells is higher. The PBE-MBD@rsSCS/FI and PBE-D3(BJ) functional give similar results in both P(1 × 1) and p(2 × 2) models, except the PBE-D3 interaction energies are larger.

It is noted that the interaction for vibrationally excited CO with the NaCl surface is much stronger than that for vibrationless CO. More importantly, the C-down configuration prevailed near the CO equilibrium geometry that is no longer the most stable. This is likely due to the peculiar feature of CO ES properties. For the CO molecule at its equilibrium geometry, the dipole moment is 0.12 D in a direction of C\textsuperscript{6+}O\textsuperscript{6+}. When r\textsubscript{CO} is increased to 1.596 Å, the dipole moment changes its direction to C\textsuperscript{6+}O\textsuperscript{6−}, and it has a much larger value of 1.14 D (calculated at the AE-CCSD(T)/aug-cc-pCVQZ level). This explains why the interaction of a stretched CO molecule with the NaCl(100) surface is much stronger than that of equilibrium CO. This change of the CO dipole with the molecule with the NaCl(100) surface is much stronger than the NaCl(100) surface, which is displayed as dashed lines in Figure 8. The isomerization barrier height is 943.2 cm\textsuperscript{−1} on the 1 × 1-MBD PES, and 1080.6 cm\textsuperscript{−1} on the 2 × 2-MBD PES, which are 94.8 and 378.7 cm\textsuperscript{−1} higher than the diffusion/isomerization paths, for the two PESs, respectively.

It is seen from Tables 1 and 3 that the vibrational frequency of CO shows a small blue shift at the C-down minima, and a small red shift at the O-down minima, in both the p(1 × 1) (1 ML) and p(2 × 2) (1/4 ML) models. These frequency shifts are responsible for the switch of energy order of the two configurations at highly excited CO vibrational states. To illustrate this point, the vibrationally adiabatic potential energy curves (V\textsubscript{p}) along the isomerization reaction paths for different CO vibrational quantum numbers (\nu) up to 40 are calculated, assuming the center-of-mass of CO is fixed at the Na\textsuperscript{+} site. These curves are generated by computing the vibrational bound states at each tilt angle on a one-dimensional PEC of CO, which is obtained from varying r\textsubscript{CO} of the corresponding point along the MEP and optimizing dZ on the full-dimensional PES, with tilt and azimuthal angles fixed at the original value and center-of-mass of CO fixed at the Na\textsuperscript{+} site. From Figure 9, one can see that, with the increase of the vibrational quantum number, the energy difference between O-down and C-down structures decreases. At \nu = 30, the O-down structure becomes more energetically favorable than its C-down counterpart. This provides the energetic driving force for the flipping of vibrationally excited CO adsorbate observed in the experiment. The barrier height separating the C-down and O-down minima also decreases as the vibrational quantum number increases, consistent with the PES landscape of stretched CO (Figure 7). Results on the 2 × 2-MBD PES and the 1 × 1-MBD PES are qualitatively similar to each other. This observation is consistent with experimentally observed trends. Quantitatively, the CO frequency shifts for the C-down and O-down configurations are +4.9 and −7.5 cm\textsuperscript{−1}, using the p(1 × 1) model with the PBE-MBD@rsSCS/FI functional for ^13\text{C}O, which can be compared with the experimental values of +7.6 and −9.3 cm\textsuperscript{−1}. A complete list of frequency shifts at various C-down and O-down configurations is given in Table 4.

Figure 8. Minimum energy paths connecting the C-down and O-down minima on the 1 × 1-MBD and 2 × 2-MBD PESs. The dashed lines correspond to the center-of-mass of CO fixed at the Na\textsuperscript{+} site.
It is interesting to note that the $v$-dependent isomerization potentials shown in Figure 9 are qualitatively consistent with the results of a simple model that only considers the ES interactions of CO fixed at a position above the surface with the electric field generated by the NaCl substrate. The predominant ES interaction leading to the change of the energy order of the C-down and O-down configurations was attributed to the switch of the CO dipole as a function of the vibrational excitation. This simple model underscores the dominant nature of the CO−NaCl ES interaction, but unfortunately, it cannot be used to describe the actual dynamics of isomerization due to the absence of vdW interactions and short-range repulsion. The DFT PESs developed in this work contain ES, vdW, and short-range interactions and are thus amenable to characterization of not only adsorption, but also isomerization dynamics.

IV. CONCLUSIONS

The PESs constructed from vdW-corrected functionals provide valuable insights into the adsorption and isomerization of CO molecules on NaCl(100). The general features of the experimentally observed $p(2 \times 1)$ CO adsorption pattern and the adsorption energy are reasonably reproduced. The PESs reveal a rather flat energy landscape near the equilibrium adsorption geometry, stemming apparently from the weak adsorbate−adsorbate and adsorbate−substrate interactions.

Concerning the isomerization of vibrationally excited CO, the PESs clearly show the C-down and O-down potential minima and the isomerization pathway between them. They also qualitatively reproduce the frequency shifts in the C-down and O-down configurations and confirm them as the origin of the flipping of the vibrationally excited CO adsorbate.

Despite the insights they provide, however, these PESs reported in this work cannot be directly used to model the experiment conducted for a monolayer of CO in the $p(2 \times 1)$ structure before vibrational excitation. This is due to the enforced periodicity in these PESs, which requires the adjacent adsorbates to have the same position, orientation, and vibrational excitation as the ones in the unit cell. This is obviously not the situation in the experiment, where a highly excited CO is most likely surrounded by coadsorbates with potentially different coordinates and orientations, as well as no or low vibrational excitations. However, the PESs represent the first step toward a realistic simulation of the experiment. To that end, we envisage a sufficiently large unit cell in which one or few vibrationally excited CO adsorbates are surrounded by multiple CO adsorbates that are mostly in their low-lying vibrational states. Thanks to the weak interacting nature of the system, the total interaction energy can in principle be decomposed into pairwise molecule−molecule and molecule−surface interactions, with negligible many-body terms. The former can be constructed with two isolated CO molecules, as we did recently, accounting for...
both the short-range vdW and long-range electrostatic interactions. The latter can be obtained using the \( p(2 \times 2) \) model or a model with an even larger surface unit cell, in which the interaction among the CO adsorbates is practically zero. Work in this direction is already underway. Once such a composite PES becomes available, we can start to simulate the energy transfer as well as the isomerization dynamics.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c05985.

Additional results including convergence test, fitting error distribution, and illustration of configurations (PDF)

- 1 × 1 MBD PES minimum energy path (MOV)
- 2 × 2 MBD PES minimum energy path (MOV)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Ewing, G. E. Energy flow from excited molecules on salt surfaces. *Acc. Chem. Res.* 1992, 25, 292–299.

(2) Hardy, J. P.; Ewing, G. E.; Stables, R.; Simpson, C. J. S. M. Thermodynamic measurements of adsorption of Xe and CO on NaCl(100). *Surf. Sci.* 1985, 159, L474–L482.

(3) Richardson, H. H.; Baumann, C.; Ewing, G. E. Infrared spectroscopy and thermodynamic measurements of CO on NaCl films. *Surf. Sci.* 1987, 185, 15–35.

(4) Richardson, H. H.; Ewing, G. E. Infrared spectrum of carbon monoxide on sodium chloride(100). *J. Phys. Chem.* 1987, 91, 5833–5835.

(5) Picaud, S.; Hoang, P. N. M.; Girardet, C.; Meredith, A.; Stone, A. J. Theoretical study of the monolayer structures of CO adsorbed on NaCl(100). *Surf. Sci.* 1993, 294, 149–160.

(6) Meredith, A. W.; Stone, A. J. A perturbation theory study of adlayer CO on NaCl(100). *J. Chem. Phys.* 1996, 104, 3058–3070.

(7) Hoang, P. N. M.; Picaud, S.; Girardet, C.; Meredith, A. W. Structure of CO monolayer adsorbed on NaCl(100) from molecular dynamics. *J. Chem. Phys.* 1996, 105, 8453–8462.

(8) Vu, N. T.; Jakalian, A.; Jack, D. B. A simulation of the phase transition in monolayer CO/NaCl(001). *J. Chem. Phys.* 1997, 106, 2551–2554.

(9) Boese, A. D.; Saalfrank, P. CO molecules on a NaCl(100) surface: Structures, energetics, and vibrational Davydov splittings at various coverages. *J. Phys. Chem. C* 2016, 120, 12637–12653.

(10) Schmicker, D.; Toennies, J. P.; Vollmer, R.; Weiss, H. Monolayer structures of carbon monoxide adsorbed on sodium chloride: A helium atom diffraction study. *J. Chem. Phys.* 1991, 95, 9412–9415.

(11) Heidberg, J.; Kampshoff, E.; Suhren, M. Correlation field, structure, and phase transition in the monolayer CO adsorbed on NaCl(100) as revealed from polarization Fourier-transform infrared spectroscopy. *J. Chem. Phys.* 1991, 95, 9408–9411.

(12) Vogt, J.; Vogt, B. The structure of carbon monoxide adsorbed on the NaCl(100) surface—A combined LEED and DFT-D/vdW-DF study. *J. Chem. Phys.* 2014, 141, 214708.

(13) Chang, H. C.; Noda, C.; Ewing, G. E. CO on NaCl(100): Model system for investigating vibrational energy flow. *J. Vac. Sci. Technol., A* 1990, 8, 2644–2648.

(14) Chang, H.-C.; Ewing, G. E. Infrared fluorescence from a monolayer of CO on NaCl(100). *Phys. Rev. Lett.* 1990, 65, 2125–2128.

(15) Chang, H. C.; Ewing, G. E. Vibrational energy transfer and population inversion in carbon monoxide overlayers on sodium chloride (100). *J. Phys. Chem.* 1990, 94, 7635–7641.

(16) Corcelli, S. A.; Tully, J. C. Vibrational energy pooling in CO on NaCl(100): Methods. *J. Chem. Phys.* 2002, 116, 8079–8092.

(17) Corcelli, S. A.; Tully, J. C. Vibrational Energy Pooling in CO on NaCl(100): Simulation and Isotope Effects. *J. Phys. Chem. A* 2002, 106, 10849–10860.

(18) Boney, E. T. D.; Marcus, R. A. On the infrared fluorescence of monolayer CO:NaCl(100). *J. Chem. Phys.* 2013, 139, 184712.

(19) Boney, E. T. D.; Marcus, R. A. Theory of vibrational equilibria and pooling at solid-diatomic interfaces. *J. Chem. Phys.* 2013, 139, 124107.

(20) Chen, L.; Lau, J. A.; Schwarzer, D.; Meyer, J.; Verma, V. B.; Wodtke, A. M. The Sommerfeld ground-wave limit for a molecule adsorbed at a surface. *Science* 2019, 363, 158–161.

(21) Lau, J. A.; Choudhury, A.; Li, C.; Schwarzer, D.; Verma, V. B.; Wodtke, A. M. Observation of an isomerizing double-Well quantum system in the condensed phase. *Science* 2020, 367, 175–178.

(22) Treanor, C. E.; Rich, J. W.; Rehm, R. G. Vibrational relaxation of anharmonic oscillators with exchange-dominated collisions. *J. Chem. Phys.* 1968, 48, 1798–1807.

(23) Powell, H. T. Vibrational relaxation of carbon monoxide using a pulse discharge. II. T = 100, 300, 500 K. *J. Chem. Phys.* 1975, 63, 2635–2645.

(24) Brechignac, P. Near-resonant V-V transfer rates for high-lying vibrational states of CO. *Chem. Phys.* 1978, 34, 119–134.

(25) DeLeon, R. L.; Rich, J. W. Vibrational energy exchange rates in carbon monoxide. *Chem. Phys.* 1986, 107, 283–292.
(26) Bohn, W.; Buelow, H. v.; Dass, S.; Ionin, A. A.; Klimachev, Y. M.; Kotkov, A. A.; McClyver, J. K.; McCord, J. E.; Slezenev, L. V.; Sinitsyn, D. V.; et al. High-power supersonic CO laser on fundamental and overtone transitions. Quantum Electron. 2005, 35, 1126–1130.
(27) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using plane wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(28) Kresse, G.; Furthmüller, J. Efficiency of ab initio total energy calculations for metals and semiconductors using plane wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(29) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(30) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.
(31) Grimme, S.; Lebègue, S.; Angyan, J. G.; Bučko, T. A fractionally ionic approach to polarizability and van der Waals many-body dispersion calculations. J. Chem. Theory Comput. 2016, 12, 5920–5930.
(32) Barrett, W. T.; Wallace, W. E. Studies of NaCl-KCl solid solutions. I. Heats of formation, lattice spacings, densities, schottky defects and mutual solubilities. J. Am. Chem. Soc. 1954, 76, 366–369.
(33) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953–17979.
(34) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 1976, 13, 5188–5192.
(35) Chen, J.; Xu, X.; Xu, X.; Zhang, D. H. A global potential energy surface for the H₂ + O₂ ↔ H₂O + H reaction using neural networks. J. Chem. Phys. 2013, 138, 154301.
(36) Jiang, B.; Li, J.; Guo, H. Potential energy surfaces from high fidelity fitting of ab initio points: The permutation invariant polynomial-neural network approach. Int. Rev. Phys. Chem. 2016, 35, 479–506.
(37) Fu, B.; Zhang, D. H. Ab initio potential energy surfaces and quantum dynamics for polyatomic bimolecular reactions. J. Chem. Theory Comput. 2018, 14, 2289–2303.
(38) Hagan, M. T.; Menhaj, M. B. Training feedforward networks with the Marquardt algorithm. IEEE Trans. Neural Networks 1994, 5, 989–993.
(39) Sarle, W. S. Stopped training and other remedies for overfitting. In Proceedings of the 27th Symposium on the Interface of Computing Science and Statistics; Interface Foundation of North America, 1995; pp 352–360.
(40) Libisch, F.; Huang, C.; Carter, E. A. Embedded correlated wavefunction schemes: Theory and applications. Acc. Chem. Res. 2014, 47, 2768–2775.
(41) Ni, Z.; Li, W.; Li, S. Fully optimized implementation of the cluster-in-molecule local correlation approach for electron correlation calculations of large systems. J. Comput. Chem. 2019, 40, 1130–1140.
(42) Nandi, A.; Bowman, J. M. Private communication.
(43) Chen, J.; Li, J.; Bowman, J. M.; Guo, H. Energy transfer between vibrationally excited carbon monoxide based on a highly accurate six-dimensional potential energy surface. J. Chem. Phys. 2020, 153, 054310.