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Theoretical Insights into the Vibrational Structure of Carbon Dioxide Rare-Gas Complexes

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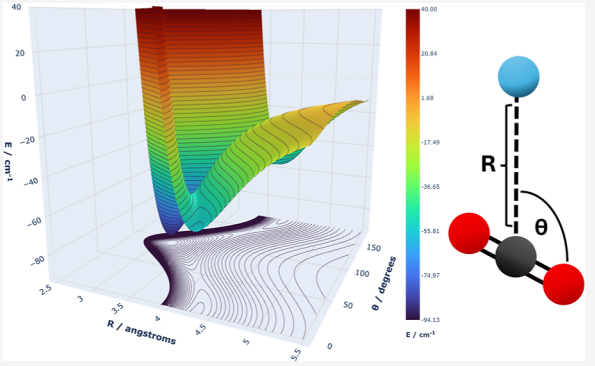
ABSTRACT: Two new flexible-monomer two-body ab initio potential energy surfaces (PESs) for the neon and krypton van der Waals complexes with carbon dioxide were developed extending our previous work on the Ar−CO_2 molecule. The accuracy of the PESs was validated by their agreement with the vibrational spectrum of the rare-gas complexes. The intermolecular and intramolecular vibrational excitation energies were computed at the vibrational self-consistent field and vibrational configuration interaction levels of theory. Overall, the agreement between theory and experiment is excellent throughout the vibrational spectra. The observed slight splitting of the bending modes, resulting from their nondegeneracy in the complexes, is confirmed by our computations, and the results qualitatively agree with the experiment. The splitting increases with increasing polarizability of the rare-gas atom. Additionally, we explain a discrepancy in the mode assignment in the intermolecular region of the neon complex with our VCI character assignment.



1. INTRODUCTION

Carbon dioxide and its van der Waals complexes play a pivotal role in atmospheric and environmental chemistry, leading to extensive experimental and theoretical studies. This widespread interest in the role of CO_2 naturally extends to its interactions in van der Waals complexes, such as argon−carbon dioxide (Ar−CO_2), neon−carbon dioxide (Ne−CO_2), and krypton−carbon dioxide (Kr−CO_2), where unique weak intermolecular interactions emerge. These interactions lead to minimum energy structures in the classic C_{2v} T-shaped configuration, which has been observed experimentally for each of the complexes.[1] Additionally, vibrational spectroscopy, especially infrared spectroscopy, has been an invaluable tool in probing these subtle interactions through the investigation of the potential energy surface (PES) and dynamics of the chemical complexes. Understanding these molecular interactions is not just of academic interest but also pivotal in comprehending the importance of carbon dioxide in climate phenomena like the greenhouse effect.

Utilizing vibrational spectroscopy, our study delves into the detailed vibrational structure of the Ne−CO_2 and Kr−CO_2 complexes, which exhibit nuanced differences from the isolated carbon dioxide molecule. Investigations of the rare-gas carbon dioxide complexes mostly emphasize van der Waals interactions, specifically the two fundamental vibrations in the intermolecular region: the bending mode and the stretching mode. For the neon complex, these frequencies have been observed at 17.9 and 38.6 cm^{-1}, respectively.[2] For krypton, the van der Waals bend and stretch energy levels were reported at 29.4 and 34.4 cm^{-1}, respectively.[2−4] Similarly, recent theoretical studies align with these experimental findings.[5] Importantly, the intramolecular frequency shifts within these complexes have been a focus of exploration. The splitting of the degenerate intramolecular bending modes was shown experimentally for the rare-gas complexes. This splitting appears to increase with increasing polarizability of the molecule, and the in-plane bend was consistently found to be lower in energy than the out-of-plane bend. Specifically, for the Ne−CO_2 complex, the splitting was determined to be approximately 0.2 cm^{-1}, and for the Kr−CO_2 complex, the splitting was observed to be about 1.5 cm^{-1}. Previously for the Ar−CO_2 complex, we found a similar splitting of the bending modes to be quite close to the experimental results of 0.8 cm^{-1}.[6] Lastly, Fermi resonance can be observed experimentally for each rare-gas carbon dioxide complex contributing to a comprehensive understanding of the vibrational dynamics in noble gas-carbon dioxide complexes.

To achieve accurate vibrational structure predictions, a precise PES is essential. Previously, permutationally invariant polynomials have been developed and implemented to

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Table 1. Fitting Accuracy for the Rg−CO_2 Two-Body Energy Function[a]

		configs.	RMSE	RMSE low	χ^2	MAX	MAX low
Ne	training set	41,354	0.8488	4.998×10^{-6}	3.3543	69.330	0.01507
	test set	10,234	0.8088	1.280×10^{-6}		69.545	0.01511
Kr	training set	41,833	2.8785	6.968×10^{-5}	35.681	78.288	0.07903
	test set	10,358	2.8093	1.751×10^{-5}		73.188	0.04008

[a]The root-mean-squared error (RMSE), mean absolute error, and maximum errors are shown over the entire training and test set and for the low-energy configurations of each in units of kcal mol^{-1}. The χ^2 value has units of (kcal mol^{-1})^2. The low parameters only include structures with energies within the ΔE range.

generate such surfaces.[7−9] In our prior work, we utilized permutationally invariant polynomials fitted to electronic structure energies computed at the CCSD(T)-F12b level of theory with the aug-cc-pVTZ basis set to enable the development of a flexible-monomer two-body potential function for carbon dioxide argon dimer.[6] A similar functional form was also established for both CO_2 monomers and dimers.[10] The accuracy of these potential energy functions (PEFs) was validated through vibrational structure computations for the CO_2 monomer, dimer, and trimer, as well as Ar−CO_2 dimer.[6] Our predicted data exhibited excellent agreement with experimental band assignments and energy levels for each molecular system. Notably, our model demonstrated remarkable precision in predicting the Fermi dyad peaks in the intramolecular region, the mode−mode coupling of the vibrations in the low-frequency intermolecular region, and the splitting of bending modes in the Ar−CO_2 complex.[6] Furthermore, our model successfully assigned vibrational frequencies that were previously poorly characterized experimentally, as was the case for the cyclic trimer.

The accuracy of the theoretical vibrational energy levels is governed by the choice of the vibrational structure approach. Typically, a hierarchy of vibrational structure methods—including the harmonic approximation, vibrational self-consistent field (VSCF) theory, and vibrational configuration interaction (VCI) theory—is applied to ensure the convergence of the vibrational energy levels by more rigorously solving the vibrational Hamiltonian.[11] Combined, an accurate PEF and hierarchical vibrational structure methods can be used to simulate the vibrational spectrum of the chemical system with accuracy compared to the experiment. In this article, we develop two new flexible-monomer two-body PESs using a model function constructed from permutationally invariant polynomials. These functions are trained on ab initio reference energies of the Ne−CO_2 and Kr−CO_2 complexes. We then employ the PEFs into the vibrational Hamiltonian and determine vibrational energy levels solved at the VSCF and VCI levels of theory.

2. COMPUTATIONAL DETAILS

2.1. Potential Energy Surface. Previously, we developed a PEF of CO_2−Ar using permutationally invariant polynomials fit to the electronic energies of the carbon dioxide monomer and the argon−carbon dioxide dimer.[6] Currently, we extend this approach to investigate the rare-gas−carbon dioxide complexes of neon and krypton. The intramolecular degrees of freedom of the carbon dioxide molecule were modeled by a one-body PEF fit to over 170,000 configurations of CO_2 monomers computed at the CCSD(T)-F12b level of theory with the aug-cc-pVTZ basis set using a sixth-degree symmetrized polynomial function. For further details on the one-body PEF and the training set used to generate it, readers are encouraged to consult our prior publication.[10] In the current work, we develop the two-body PEF for the Rg−CO_2 dimers by using a fifth-degree polynomial function consisting of intramolecular and intermolecular exponential functions for each of the six interatomic distances in each complex. These two-body PEFs are built from a linear combination of 222 unique symmetrized polynomials, which not only account for the intermolecular dynamics in the Rg−CO_2 complex but also for the intramolecular degrees of freedom of the CO_2 molecule. The entire model function can be found in the authors' GitHub repository.

For each rare-gas complex, a training set of at least 41,000 unique configurations was computed at the CCSD(T)-F12b/aug-cc-pVTZ level of theory and basis set with the Molpro software package.[12] The training set was generated through projections along the fundamental and combination vibrational modes. Both the intermolecular and intramolecular degrees of freedom were considered for each molecule at the global minimum energy (T-shaped) structure and transition-state (linear) structure. Additional configurations were generated using a three-dimensional grid, whose coordinates included the intermolecular stretch distance, the intermolecular bend angle, and the intramolecular symmetric stretch of each molecule. In this way, configurations further from the energy minimums were explored. Lastly, configurations where the atomic coordinates were randomly perturbed were also incorporated into each training set. These can be found in the authors' GitHub repository.

The training sets were used to fit the flexible-monomer two-body PEF. Linear and nonlinear coefficients were optimized via Tikhonov regularization,[13] minimizing the weighted sum of the squared errors according to the following equation

$$\chi^2 = \sum_n w_n [V^{\text{model}}(n) - V^{\text{ref}}(n)]^2 + \Gamma \sum_k c_k^2 \quad (1)$$

Here, k runs over the list of linear coefficients, n runs over the list of training set configurations, and Γ represents the regularization term, set to 5.0×10^{-2}, which mitigates overfitting. The model and reference energies for the nth configuration are given as $V^{\text{model}}(n)$ and $V^{\text{ref}}(n)$, respectively. The weighting factor (w_n), which stresses configurations with lower total energies, is expressed as

$$w(E) = \left(\frac{\Delta E}{E - E_{\text{min}} + \Delta E} \right)^2 \quad (2)$$

where E_{min} is the minimum energy value and ΔE, set to 10 kcal mol^{-1}, is the energy range for selecting the subset of emphasized configurations.

The fits of each model potential with respect to the reference energies, as shown in Table 1, are very accurate, especially in the low-energy range. Here, the largest deviation

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from the test set energies was 0.01511 and 0.04008 kcal mol^{-1} for Ne and Kr, respectively. More than 10,000 configurations were used for the test set for each model potential, and notably, the root-mean-squared error (RMSE) and maximum error were comparable in the training and the test sets.

2.2. Vibrational Schrödinger Equation. The rare-gas−carbon dioxide complex PESs are included in a vibrational Hamiltonian with general curvilinear coordinates. This Hamiltonian is separable and can be decomposed into its kinetic energy and potential energy terms.[14,15] In this article, we employ the notation introduced by Strobusch and Scheurer[14,15] to refer to the many-body expansion orders for Hamiltonian terms, as $V(O_V)/T(O_M, O_K, O_{\nabla G}, O_{V_g})$. These components refer to the potential energy term (V), on-diagonal (M) and off-diagonal (K) elements of the kinetic energy operator G matrix terms, the ∇G term, and the pseudopotential term, commonly denoted as V_g. For the Rg−CO_2 complexes, we employ a reduced-dimensional vibrational Hamiltonian, $V(3)/T(3,3,3,3)$. We previously reported the convergence of vibrational frequencies using the VSCF approach compared to the full expansion, $V(6)/T(6,6,6,6,6)$ for the Ar−CO_2.[6]

We employ the VSCF[16−19] and the VCI approaches[20−22] to solve the vibrational Schrödinger equation. The harmonic approximation solutions are also reported within the NITROGEN software package.[23] The VSCF approach is exact only when the Hamiltonian is additively separable and defines solutions to the Schrödinger equation wave functions as products of one-mode functions. The VCI calculations explicitly consider mode−mode interactions, which can be quantified by analyzing the wave function contributions. In this work, only configurations with a maximum sum of VCI quanta less than 15 (a total of 38,760 VSCF configurations) were considered. At this level, the vibrational frequencies are well converged. All excited state energies and VCI configuration amplitudes can be found in the authors' GitHub repository (http://github.com/sodelab).

3. RESULTS AND DISCUSSION

3.1. Structural Parameters. The ground-state global minimum energy structure of each Rg−CO_2 complex was found to be T-shaped (θ = 90.0°), as shown in Table 2. The intermolecular distance, R, for the neon complex was found to be 3.150 Å at the global minimum, and for the krypton complex, R was determined as 3.596 Å. Previously for the for Ar−CO_2 complex, the minimum energy intermolecular distance was found between these two values.[6] Additionally, our optimized structural parameters agree quite well with the experiment. For the neon complex, the experiment shows this intermolecular distance at 3.2904 Å, and for krypton complex, the distance is 3.6243 Å.[1] The angles are slightly less than 90.0° in both the neon and krypton complexes−81.42 and 83.28°, respectively. As is noted in previous studies, the computed parameters reflect the equilibrium structure of each Rg−CO_2 complex, whereas the experimental values represent the zero-point energy structure. We also show good agreement with respect to the other theoretical studies.[5,24−26] We also present the well depths for the neon and krypton complexes, which are −89.02 and −213.34 cm^{-1}, respectively. Notably, our PES is capable of treating the intramolecular carbon−oxygen distance of the complexes, and in each case, the minimum energy structure is found to have a intramolecular distance (r_{CO}) equal to 1.1622 Å.

A local energy-minimum linear structure is found for each complex, similar to the argon complex. Notably, no experiment has found the stable linear structure. Here, the intermolecular distances in the neon and krypton complexes are found to be 4.304 and 4.770 Å, respectively, and the well depths for these compounds are −55.22 and −124.25 cm^{-1}, respectively. The intramolecular r_{CO} bonds remain unchanged for the neon complex (1.1622 Å) but are slightly larger on average in the case of krypton (1.1623 Å). For comparison, our previous Ar−CO_2 linear complex results indicate a carbon−argon distance of 4.620 Å, an intramolecular r_{CO} bond distance of 1.1623, and a well depth of −115.42 cm^{-1}.[6]

3.2. Neon Intermolecular Vibrational Frequency Region. We present the first five intermolecular vibrations for the T-shaped Ne−CO_2 complex in Table 3. We employ three levels of increasingly accurate vibrational structure methods (i.e., the harmonic approximation, VSCF and VCI) and present the results alongside experimental and theoretical values from the literature. Two fundamental modes exist in this region: the intermolecular bend (ν_b) and the intermolecular stretch (ν_s). At each level of theory, the bend mode is found to have a lower excitation energy than the stretch mode, which corresponds to what was shown previously for the Ar−CO_2 complex.[6] At the VCI level, the bend frequency is found to be 17.76 cm^{-1}, compared to 17.9 and 17.716 cm^{-1}, experimentally.[1,2,27] This agreement shows the accuracy of the vibrational approximation and the PES. The stretch frequency is found at 23.91 cm^{-1} at the VCI level and, similar to the bend mode, relaxes at higher levels of theory. Chen et al. report theoretical

Table 2. Structural Parameters of the Ground-State Minimum of the Ne−CO_2, Ar−CO_2, and Kr−CO_2 Complexes[a]

		R	θ	r_{CO}	energy
Ne	Chen et al.[24]	3.15	90.0		−93.05
	this work	3.150	90.0	1.1622	−89.02
	experiment[1]	3.2904	81.42		
Ar	Cui et al.[25]	3.440	90.0		−200.97
	Zhao et al.[26]	3.432	90.0		−199.38
	previous work	3.436	90.0	1.1622	−195.96
	experiment[1]	3.5039	83.10		
Kr	Chen et al.[5]	3.57	90.0		−231.70
	this work	3.596	90.0	1.1622	−213.34
	experiment[1]	3.6243	83.28		

[a]The intermolecular distance between the Rg and CO_2, R, and the average intramolecular CO_2 distance between C and O atoms, r_{CO}, are reported in angstroms. The angle θ is reported in degrees. The well depth is reported in cm^{-1}.

Table 3. Intermolecular Vibrational Energy Levels (in cm^{-1}) of the Ne−CO_2 Complex Obtained with the Harmonic Approximation, VSCF, and VCI Methods Are Compared to Experimental and Theoretical Values from the Literature

	HAR	VSCF	VCI	expt.[1,2,27]	Chen et al.[24]
ν_b	25.37	19.84	17.76	17.9, 17.716	17.94
ν_s	39.69	28.48	23.91	38.6	23.19
$2\nu_b$		36.89	36.22		
$\nu_b + \nu_s$		45.35	37.58		
$2\nu_s$		49.33	44.18		

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intermolecular bend and stretch excitation energies at 17.94 and 23.19 cm^{-1}, respectively, which match exceptionally well with our computed results. Interestingly, both theoretical results for the stretch frequency disagree with the experimentally determined value previously reported. We will address this disagreement by looking at the combination bands in the intermolecular region and by re-emphasizing that the experimentally determined vibrational excitation energies in this region are obtained through combination bands in the CO_2 intramolecular asymmetric stretching region. These intramolecular and intermolecular combination modes will be explored in the following section.

Additionally, we report three overtone and combination vibrational frequencies in this region of the complex in Table 3. At the VCI level, we see the intermolecular bend overtone ($2\nu_b$), the bend and stretch combination ($\nu_b + \nu_s$), and the intermolecular stretch overtone ($2\nu_s$) at 36.22, 37.58, and 44.18 cm^{-1}, respectively. Interestingly, the coefficients of the VCI wave function for the bending overtone point toward the explanation for the assignment discrepancy between the experiment and theory.

$$\Psi_{2\nu_b}^{VCI} = 0.596\Psi_{\nu_s}^{VSCF} + 0.522\Psi_{2\nu_b}^{VSCF} + \cdots \quad (3)$$

The leading VSCF mode contribution to the mode we have labeled as the intermolecular bend overtone ($2\nu_b$) is in fact the van der Waals stretch fundamental ($\Psi_{\nu_s}^{VSCF}$). Thus, it might make more sense to label this mode as another van der Waals stretch. It should also be noted that the van der Waals stretch frequency at 23.91 cm^{-1} ($\Psi_{\nu_s}^{VCI}$) also has intermolecular bend overtone character but to a lesser degree. This combined character makes simple assignment of the modes in this region difficult. However, it also helps explain why we see the experimental assignment of the intermolecular stretch around 38 cm^{-1} since this peak does in fact contain van der Waals stretch character. Vibrational mode assignment in the complex will be explored in detail further in the intramolecular region, in particular as it relates to Fermi resonance and the intramolecular bending mode splitting.

3.3. Neon Intramolecular Vibrational Frequency Region. The intramolecular frequencies of the Ne−CO_2 complex are shown in Table 4. The first eight frequencies correspond to the intramolecular vibrations of the CO_2 in the van der Waals complex, four of which are fundamental vibrations: in-plane and out-of-plane intramolecular bends (ν_2^i and ν_2^o, respectively), symmetric stretch (ν_1), and the asymmetric stretch (ν_3). Additionally, we report combination, overtone, and Fermi dyad bands arising from these intramolecular CO_2 vibrations, as well as combinations of the asymmetric stretch intramolecular mode and the intermolecular mode vibrations. These latter values may provide additional insights into the frequencies from Table 3, especially regarding the experiment.

The two in-plane and out-of-plane intramolecular bending modes in the Ne−CO_2 complex, as shown in Table 4, are observed to have frequencies of 668.47 and 668.73 cm^{-1}, respectively, at the VCI level of theory. We found previously the degenerate bending modes of the isolated CO_2 molecule at 667.8 cm^{-1} at the same level of theory,[29] compared to 667.380 cm^{-1} experimentally.[30] The observed nondegeneracy at all levels of theory for the intramolecular bending modes is also consistently observed in the Ar−CO_2 complex. However, for the current Ne−CO_2 complex, the magnitude of the symmetry

Table 4. Intramolecular Vibrational Energy Levels (in cm^{-1}) of the Ne−CO_2 Complex Obtained with the Harmonic Approximation, VSCF, and VCI Methods[a]

	HAR	VSCF	VCI	expt.[1,3,27,28]
ν_2^i	673.18	670.46	668.47	667.380
ν_2^o	673.36	670.69	668.73	667.436
$2\nu_2^o/2\nu_2^i$			1285.53[b]	
$2\nu_2^i$		1341.08	1338.73	
$2\nu_2^o$		1341.25	1338.73	
$\nu_2^o + \nu_2^i$		1343.01	1338.71	
ν_1	1352.54	1349.54	1389.32[b]	
ν_3	2394.59	2353.59	2348.37	2349.280
$\nu_3 + \nu_b$		2373.31	2366.05	2366.9960
$\nu_3 + \nu_s$		2382.02	2372.55	
$\nu_3 + 2\nu_b$		2390.26	2385.28	
$\nu_3 + \nu_b + \nu_s$		2398.81	2386.6	
$\nu_3 + 2\nu_s$		2402.86	2393.09	
$\nu_3 + \nu_2^i$		3011.79	3004.57	3004.154
$\nu_3 + \nu_2^o$		3012.02	3004.84	3004.204
$2\nu_2^o/2\nu_2^i + \nu_3$		3670.33	3612.74[b]	3612.98919
$\nu_1 + \nu_3$		3698.98	3715.76[b]	3714.97590

[a]Note that unlike in the isolated CO_2 monomer, the bending modes, ν_2^o and ν_2^i, are no longer degenerate. [b]The Fermi dyad bands are denoted ~~with an asterisk~~.

breaking of the degenerate bend modes is about 0.2 cm^{-1} with the in-plane bend being consistently less energetic than the out-of-plane bend. This agrees with recent experimental observation showing the in-plane bend 0.057 cm^{-1} lower in energy than the out-of-plane bend. The experimental bending frequency values in Table 4 are obtained by adding this difference to the energy level of the experimentally determined isolated monomer bending mode.[27]

The remaining fundamental frequencies in this region remain mostly unchanged from the isolated CO_2 monomer. We compute the asymmetric stretch vibrational excitation in the complex as 2348.37 cm^{-1}, at the VCI level, compared to 2349.28 cm^{-1}, experimentally.[1,27] For comparison, the isolated ν_3 band in the isolated CO_2 molecule is detected at 2349.2 cm^{-1}.[30] Our theoretical results for the asymmetric stretch frequency in the complex are shown to be about one wavenumber lower in energy than the experiment. This trend was observed for the Ar−CO_2 molecule previously and holds also for the Kr−CO_2 molecule. In the symmetric stretch region, the fundamental frequency for the complex is found at 1349.54 cm^{-1}, compared to 1340.4 cm^{-1} in the isolated molecule, at the VSCF level. There is no direct comparison to the experiment (or VCI) due to its large mode mixing, characteristically known as Fermi resonance. In general, the agreement underscores the accuracy of our method across different molecular systems.

The Fermi dyad peaks found in the symmetric stretch region, denoted as $2\nu_2^o/2\nu_2^i$ and ν_1, are detected at 1285.53 and 1389.32 cm^{-1}, at the VCI level. This indicates a very weak perturbation from the isolated monomer potential with Fermi dyad peaks observed at 1284.7 and 1388.7 cm^{-1}. The Fermi mixed $2\nu_2^o/2\nu_2^i + \nu_3$ and $\nu_1 + \nu_3$ modes are observed experimentally at 3612.99 and 3714.98 cm^{-1}, which agrees quantitatively with our VCI frequencies of 3612.74 and 3715.76 cm^{-1}, respectively.[3]

Due to the complete PES treatment of the Ne−CO_2 complex in the vibrational Schrodinger equation, we can

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evaluate the combination bands between intermolecular and intramolecular interactions in the asymmetric stretching region and compare these values to the intermolecular mode frequencies in Table 4. The ordering for the combination modes follows that of the intermolecular modes: ν_b, ν_s, $2\nu_b$, $\nu_b + \nu_s$, and $2\nu_s$. The largest deviation in energy amounts to about 0.7 cm^{-1}, which further justifies the reduced dimensional treatment.

3.4. Krypton Intermolecular Vibrational Frequency Region.

The first five intermolecular vibrations for the T-shaped Kr−CO_2 complex are shown in Table 5. As with the neon complex, we report the vibrational excitation energies at the harmonic approximation, VSCF, and VCI levels theory alongside experimental and theoretical values from the literature. Again, the van der Waals bend fundamental is consistently lower in energy than the van der Waals stretch frequency at all levels of theory. At the VCI level, the difference between the bend and stretch frequencies is 2.77 cm^{-1}. This matches with the differences observed experimentally of 2.80 and >2.5 cm^{-1},[2,4] however, our computed results are shifted lower in energy by about 2 cm^{-1} compared to the experiment. Chen et al. report the two fundamental intermolecular frequencies at 30.027 and 32.233 cm^{-1} for the bend and stretch, respectively.[5] Conversely, the empirically determined stretch frequency found at 42.4 cm^{-1} seems to be an outlier compared to the other computed and detected values.[3]

Table 5. Intermolecular Vibrational Energy Levels (in cm^{-1}) of the Kr−CO_2 Complex Obtained with the Harmonic Approximation, VSCF, and VCI Methods Are Compared to Experimental and Theoretical Values from the Literature

	HAR	VSCF	VCI	expt.[2−4]	Chen et al.[5]
ν_b	32.00	29.25	27.60	31.6, 29.429	30.027
ν_s	35.98	32.74	30.37	34.4, 42.4	32.233
$2\nu_b$		55.7	52.79		
$\nu_b + \nu_s$		61.1	53.20		
$2\nu_s$		62.18	58.53		

We report the combination and overtone frequencies for this region, as well, and observe the same ordering as the neon complex: the bending overtone, the stretch and bend combination, and the stretch overtone. The VCI level of theory relaxes the computed VSCF excitation energies as they are observed at 52.79, 53.20, and 58.53 cm^{-1}, respectively. To our knowledge, no direct experimental observations have been made for these frequencies. Next, we will explore in detail the vibrational frequencies in the intramolecular region.

3.5. Krypton Intramolecular Vibrational Frequency Region.

The intramolecular vibrational frequencies for the Kr−CO_2 complex are reported in Table 6. Again, the four CO_2 fundamental vibrations (in-plane and out-of-plane intramolecular bends, symmetric stretch, and the asymmetric stretch) are shown, alongside the other intramolecular modes, including the Fermi dyad and other combination bands involving the intermolecular motions of the complex.

In the intramolecular bend region of the vibrational spectrum, we observe the same relative ordering of the in-plane and out-of-plane vibrations compared to the other rare-gas complexes: the in-plane bend found at 666.68 cm^{-1} is less energetic than the out-of-plane bend observed at 668.58 cm^{-1}. However, the splitting here is much larger than that for the other molecules. Table 7 shows the experimental and theoretical CO_2 ν_2 splitting values for the neon, argon, and krypton complexes.[6] For Kr−CO_2, we compute a splitting of 1.95 cm^{-1} compared to the 1.418 cm^{-1} experimentally determined value.[4]

Table 6. Intramolecular Vibrational Energy Levels (in cm^{-1}) of the Kr−CO_2 Complex Obtained via Harmonic Approximation, VSCF, and VCI Methods

	HAR	VSCF	VCI	expt.[1,3,4,28]
ν_2^i	670.68	668.60	666.58	667.380
ν_2^o	672.98	670.36	668.53	668.798
$2\nu_2^o/2\nu_2^i$			1284.39[a]	
$2\nu_2^i$		1337.41	1336.46	
$\nu_2^o + \nu_2^i$		1340.62	1336.48	
$2\nu_2^o$		1340.64	1336.46	
ν_1	1352.09	1349.22	1284.39[a]	
ν_3	2393.40	2352.59	2347.39	2348.259205
$\nu_3 + \nu_b$		2381.99	2375.09	
$\nu_3 + \nu_s$		2385.38	2377.84	
$\nu_3 + 2\nu_b$		2408.59	2400.69	
$\nu_3 + \nu_b + \nu_s$		2413.85	2401.19	
$\nu_3 + 2\nu_s$		2414.87	2406.09	
$2\nu_2^o/2\nu_2^i + \nu_3$		3668.74	1284.39[a]	3610.86796
$\nu_1 + \nu_3$		3697.68	1284.39[a]	3713.02414

[a]The Fermi dyad bands are denoted ~~with an asterisk~~.

Table 7. Experimental and Theoretical CO_2 ν_2 Splitting Values for the Rare-Gas Dimers in cm^{-1}[a]

	VCI	expt.
Ne−CO_2	0.26	0.057
Ar−CO_2[6]	0.83	0.877
Kr−CO_2	1.95	1.418

[a]For each complex, the out-of-plane bend was observed as more energetic than the in-plane bend. The theoretical values are shown at the VCI level of theory.

In the symmetric stretch region, the upper and lower Fermi dyad peaks (denoted again as $2\nu_2^o/2\nu_2^i$ and ν_1) are found at 1284.39 and 1388.21 cm^{-1}, respectively. Again, this represents a weak perturbation from the isolated monomer. Unfortunately, no experimental data exist for these assignments; however, the Fermi dyad that results from a combination band with the asymmetric mode frequency is observed. The experimental lower and upper peaks are found at 3610.87 and 3713.02 cm^{-1}, respectively, compared to our VCI frequencies at 3610.54 and 3713.67, respectively.[3] This near perfect agreement points toward the accuracy of the lower peaks.

The asymmetric stretch frequency for the complex was found at 2347.39 cm^{-1} at the VCI level, again about 1 cm^{-1} below the experimental peak.[1] In this region as well, the intermolecular combination bands were also found in the same ordering as before: ν_b, ν_s, $2\nu_b$, $\nu_b + \nu_s$, and $2\nu_s$. The difference between these combination bands and the asymmetric stretch frequency results in frequencies that closely match the intermolecular vibrational excitations before. The largest deviation in energy amounts to about 0.6 cm^{-1}, again justifying the reduced dimensional treatment.

4. CONCLUSIONS

Extending on our work in the Ar−CO_2 system, we have developed two new flexible-monomer two-body PEFs for the

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Ne−CO_2 and Kr−CO_2 systems fit to energies at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. In both molecules, as is the case for the argon complex, both the T-shaped global minimum and linear local minimum were found. The vibrational structure of both T-shaped complexes was explored using the harmonic approximation and VSCF, as well as the experimentally accurate VCI approach. The vibrational frequencies in the intermolecular and intramolecular regions were presented and compared quite accurately to experiment and previous theoretical results. In particular, for the Ne−CO_2 complex, our work was able to clarify the previous discrepancy between the theoretical and experimental frequency for the intermolecular stretch. The experimental band peak is most likely associated with a mixed vibrational motion that contains van der Waals bend overtone and van der Waals stretch character. This peak found at 38.6 cm^{-1} experimentally matches well with our peak at 36.22 cm^{-1}. In the intramolecular bending region for both molecules, the experimental trend for the splitting of the bending modes is observed. We report the out-of-plane bend frequency to be 0.26 and 1.95 cm^{-1} more energetic than the in-plane bend frequency for the neon and krypton complexes, respectively. The computed Fermi resonance peaks quantitatively agreed with the experiment in both complexes to within 1 cm^{-1} in the asymmetric stretch and symmetric stretch combination band region. Future work will explore the helium and xenon systems, and it is presently underway.

■ ASSOCIATED CONTENT

Data Availability Statement

~~Furthermore,~~ the PES and training set data are openly available in the authors' GitHub repository (https://github.com/sodelab).

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.4c00639.

Breakdown of the VCI mode contributions in the intramolecular and intermolecular regions of both complexes as well as the optimized geometries (ZIP)

Ne−CO_2 intermolecular contributions, neon intramolecular mode-mixing contributions, and Kr−CO_2 intermolecular and intermolecular mode−mode contributions (PDF)

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Notes

The authors declare no competing financial interest.

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