

 Open access • Journal Article • DOI:10.1063/1.475290

A new He-CO interaction energy surface with vibrational coordinate dependence. I. Ab initio potential and infrared spectrum — Source link

Tino G. A. Heijmen, Robert Moszynski, Paul E. S. Wormer, Ad van der Avoird

Published on: 15 Dec 1997 - Journal of Chemical Physics (American Institute of Physics)

Topics: Ab initio, Vibrational energy relaxation, Bond length, Bound state and Ab initio quantum chemistry methods

Related papers:

- [Infrared spectrum and potential energy surface of He–CO](#)
- [Ab initio potential energy surface, infrared spectrum, and second virial coefficient of the He–CO complex](#)
- [Improved modelling of atom–molecule potential-energy surfaces: illustrative application to He–CO](#)
- [Observation of strong hidden lines in the infrared spectrum of the CO–He complex](#)
- [The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/a-new-he-co-interaction-energy-surface-with-vibrational-3oskpaa3et>

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/17385>

Please be advised that this information was generated on 2022-05-29 and may be subject to change.

A new He–CO interaction energy surface with vibrational coordinate dependence. I. *Ab initio* potential and infrared spectrum

Tino G. A. Heijmen

Institute of Theoretical Chemistry, NSR Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

Robert Moszynski

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Paul E. S. Wormer and Ad van der Avoird

Institute of Theoretical Chemistry, NSR Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

(Received 20 May 1997; accepted 8 September 1997)

The intermolecular potential energy surface of the He–CO complex including the CO bond length dependence has been calculated using symmetry-adapted perturbation theory (SAPT). The potential has a minimum of $\epsilon_m = -23.734 \text{ cm}^{-1}$ with $R_m = 6.53$ bohr at a skew geometry ($\vartheta_m = 48.4^\circ$) if the molecular bond length is fixed at the equilibrium value of 2.132 bohr. We have applied the potential in the calculation of bound state levels and the infrared spectrum for the ^3He –CO and ^4He –CO complexes. The computed *ab initio* transition frequencies are found to agree within 0.1 cm^{-1} with experiment. In paper II [J. P. Reid, H. M. Quiney, and C. J. S. M. Simpson, *J. Chem. Phys.* **107**, 9929 (1997)], the potential surface is used to calculate vibrational relaxation cross sections and rate constants. © 1997 American Institute of Physics. [S0021-9606(97)03146-2]

I. INTRODUCTION

The interaction between the helium atom and the carbon monoxide molecule has been the subject of a variety of experimental and theoretical studies. The system is of interest from an astrophysical point of view on account of the role that the CO molecule plays in dense interstellar clouds. Carbon monoxide is excited mostly by collisions with abundant species such as He and H_2 in that environment. Additionally, the He–CO van der Waals complex shows interesting dynamics which lie between the semirigid and nearly free rotor limits.

The relatively small number of electrons of He–CO permits theoreticians to calculate intermolecular potential energy surfaces by *ab initio* methods. Thomas, Kraemer, and Dierksen (TKD) published a potential in 1980¹ that was calculated at the singles and doubles configuration interaction (CISD) level. Although their potential was state-of-the-art at that time, the use of rather small basis sets resulted in an underestimated potential well depth. Furthermore, the interaction energy was not corrected for the basis set superposition error (BSSE). The TKD potential was extended later² to include the dependence on the CO bond length. More recently, two *ab initio* potentials were computed by the supermolecular approach using fourth-order many-body perturbation theory (MBPT4).^{3,4} The authors of the current paper reported a preliminary potential calculated by applying symmetry-adapted perturbation theory (SAPT).⁵

A number of spectroscopic studies as well have been devoted to the He–CO complex. Chuaqui *et al.*⁶ recorded high-resolution infrared spectra near the fundamental band region of the CO monomer for the complex with ^3He and ^4He . A more powerful spectroscopic technique was applied recently⁷ to detect the “hidden” lines in the spectra, which

were obscured by transitions of the CO monomer in the original measurements. The authors of Ref. 6 could not assign all observed transitions using conventional spectroscopic methods and theoretical spectra generated from the *ab initio* TKD potential. Therefore, a two-dimensional potential energy surface named $V_{(3,3,3)}$ was fitted to reproduce the experimental transition frequencies. Subsequently, a potential with a different functional form was determined from a fit to the same set of spectroscopic data.⁸ The starting point of the new potential surface was the exchange-Coulomb (XC) model potential, which is partly based on *ab initio* information on the exchange-repulsion energy and long-range induction and dispersion coefficients. This “XC” potential reproduced the observed spectrum as well as the $V_{(3,3,3)}$ potential. Moreover, because of its sounder theoretical basis the XC potential is expected to be more realistic in the regions not sampled by the spectroscopic data.

The semi-empirical XC and $V_{(3,3,3)}$ potentials and the *ab initio* TKD and SAPT potentials were used to calculate pressure broadening and shifting cross sections for pure rotational transitions of CO in helium.⁹ Good qualitative agreement was obtained for the cross sections computed from the XC, $V_{(3,3,3)}$, and SAPT potentials. The theoretical data, however, are in substantial disagreement with experiment¹⁰ at very low temperatures. This deviation is probably due to experimental errors or the breakdown of the line-shape theory, not because of inaccuracies in the potentials. The agreement of the cross sections obtained from the TKD potential with some of the experimental very low temperature data appeared to be fortuitous. Second virial coefficients computed from the SAPT potential⁵ and from the XC and $V_{(3,3,3)}$ potentials¹¹ were in reasonable accord with experi-

mental data. The SAPT potential was also tested against experimental transport properties.¹²

Vibrational relaxation of CO ($v=1$) by inelastic collisions with helium atoms has been the subject of various theoretical studies (see paper II¹³ and references therein). Vibration relaxation strongly depends on the shape of the intermolecular potential. Rate constants determined at very low temperatures are sensitive to the van der Waals well, while the anisotropy of the repulsive wall is probed at higher temperatures. Most of the studies on vibrational relaxation rate constants of the last decade used the TKD potential.^{1,2} Since comparative studies have shown that this TKD potential suffers from inaccuracies, a high quality He-CO potential including the vibrational coordinate dependence is needed.

The current paper presents the calculation of an *ab initio* SAPT potential dependent on the CO bond length. In Ref. 5, the two-dimensional SAPT potential was used in dynamical calculations on the frequencies and intensities of the transitions in the infrared spectrum accompanying the fundamental bond of CO. It was found that the line positions agreed within a few tenths of a wave number with the experimental data from Ref. 6. To test the accuracy of the current three-dimensional potential in the region of the Van der Waals minimum a new series of dynamical calculations have been performed. The results are compared with the data from Ref. 6 as well as with the new data from Ref. 7. In the subsequent article (paper II), the three-dimensional potential is used to calculate rate constants for the vibrational relaxation of the ⁴He-CO and ³He-CO complexes.

II. OUTLINE OF SAPT CALCULATIONS

The SAPT approach used here has been described in a number of papers.^{5,14-16} The interaction energy can be decomposed into terms corresponding to the Hartree-Fock ($E_{\text{int}}^{\text{HF}}$) and correlated ($E_{\text{int}}^{\text{corr}}$) levels of theory,

$$E_{\text{int}} = E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{corr}}. \quad (1)$$

The Hartree-Fock interaction energy was obtained from supermolecular self-consistent field calculations and represented as a sum of individual contributions.¹⁷⁻²⁰ The SAPT contribution to the interaction energy at the correlated level is represented here as in Ref. 5, except that the electron correlation effects on the exact first-order exchange contribution are approximated by

$$\epsilon_{\text{exch}}^{(1)} = E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD}). \quad (2)$$

In the expression for $E_{\text{exch}}^{(12)}$ the first- and second-order cluster operators are replaced by converged coupled-cluster operators,²¹ leading to a sum of higher-order terms (in the intramolecular correlation) denoted $\Delta_{\text{exch}}^{(1)}(\text{CCSD})$. Although the CCSD correction was not included in the potential of Ref. 5, it was discussed that it may have a non-negligible effect on the anisotropy.

The interaction energy surface for the He-CO system can be naturally expressed in Jacobi coordinates (R, r, ϑ), where R is the distance between the c.m. of CO and the

helium atom, r is the CO bond length, and ϑ is the angle between the vector pointing from the molecular c.m. to the atom and the vector pointing from the carbon to the oxygen nucleus. Calculations have been performed for intermolecular distances $R=5, 6, 7, 8,$ and 10 bohr, and seven equidistant angles ϑ ranging from $\vartheta=0^\circ$ to $\vartheta=180^\circ$. In addition, potential energy curves have been computed for $\vartheta=15^\circ, 75^\circ, 105^\circ,$ and 165° . The CO bond length r was varied over five values: the equilibrium bond length $r_e=2.132$ bohr,²² the two values of $r=1.898$ and 2.234 bohr at which Schinke and Dierksen² previously calculated a potential energy surface, and two additional values of $r=2.050$ and 2.170 bohr. In total, we calculated 275 points on the three-dimensional surface.

As in our previous work,⁵ a $[5s3p2d]$ basis was used for the helium atom. The s orbitals were represented by the (61111) contraction of van Duijneveldt's $10s$ set,²³ and the exponents of the polarization functions were taken from Ref. 24. For the carbon and oxygen atoms we took the $[8s5p3d1f]$ basis sets of Dierksen and Sadlej,²⁵ optimized for the dipole and quadrupole properties of the CO molecule. In Ref. 5, however, the five steepest p functions on both C and O were inadvertently contracted to one basis function instead of two. All terms except $E_{\text{disp}}^{(20)}$ were calculated with this basis set. In the calculation of $E_{\text{disp}}^{(20)}$ an extended basis set was used with diffuse bond functions from Ref. 26, located at the middle of the intermolecular bond. To investigate the effect of the basis, we performed additional calculations at $R=7$ bohr, $r=2.132$ bohr, and $\vartheta=0^\circ$ and 180° with the $[9s7p3d2f]$ basis sets for the carbon and oxygen atoms from Hettema *et al.*²⁷ Polarization functions were applied in their spherical form (five d functions and seven f functions). Full dimer basis sets were used in the SAPT calculations in order to account for charge-overlap effects.

All calculations were performed employing the SAPT system of codes.²⁸ The POLCOR package²⁹ was used to compute additional long-range induction and dispersion coefficients corresponding to the multipole expanded induction and dispersion energies. These long-range coefficients, calculated with the same basis sets and at the same level of theory, were subsequently used in the analytical fitting of the induction and dispersion energies. The Boys-Bernardi counterpoise correction³⁰ was applied to eliminate the BSSE from the supermolecular Hartree-Fock interaction energy.

A two-step procedure was used in fitting the interaction energy. In the first step, one-dimensional fits in R were produced for each value of ϑ ; subsequently we expanded all fit parameters in Legendre polynomials $P_l(\cos \vartheta)$. The CO bond length dependence of the potential was represented by expanding the linear parameters in powers of $r-r_e$, where $r_e=2.132$ bohr is the experimental CO equilibrium bond length. In the second step, we used a global three-dimensional fitting procedure with the parameters from the one-dimensional fits of the first step as starting point. The fitted potential reproduces all *ab initio* calculated points within 2%. In the region of the potential minimum the difference between the fitted potential energy and its *ab initio* counterpart is typically a few tenths of a wave number and at

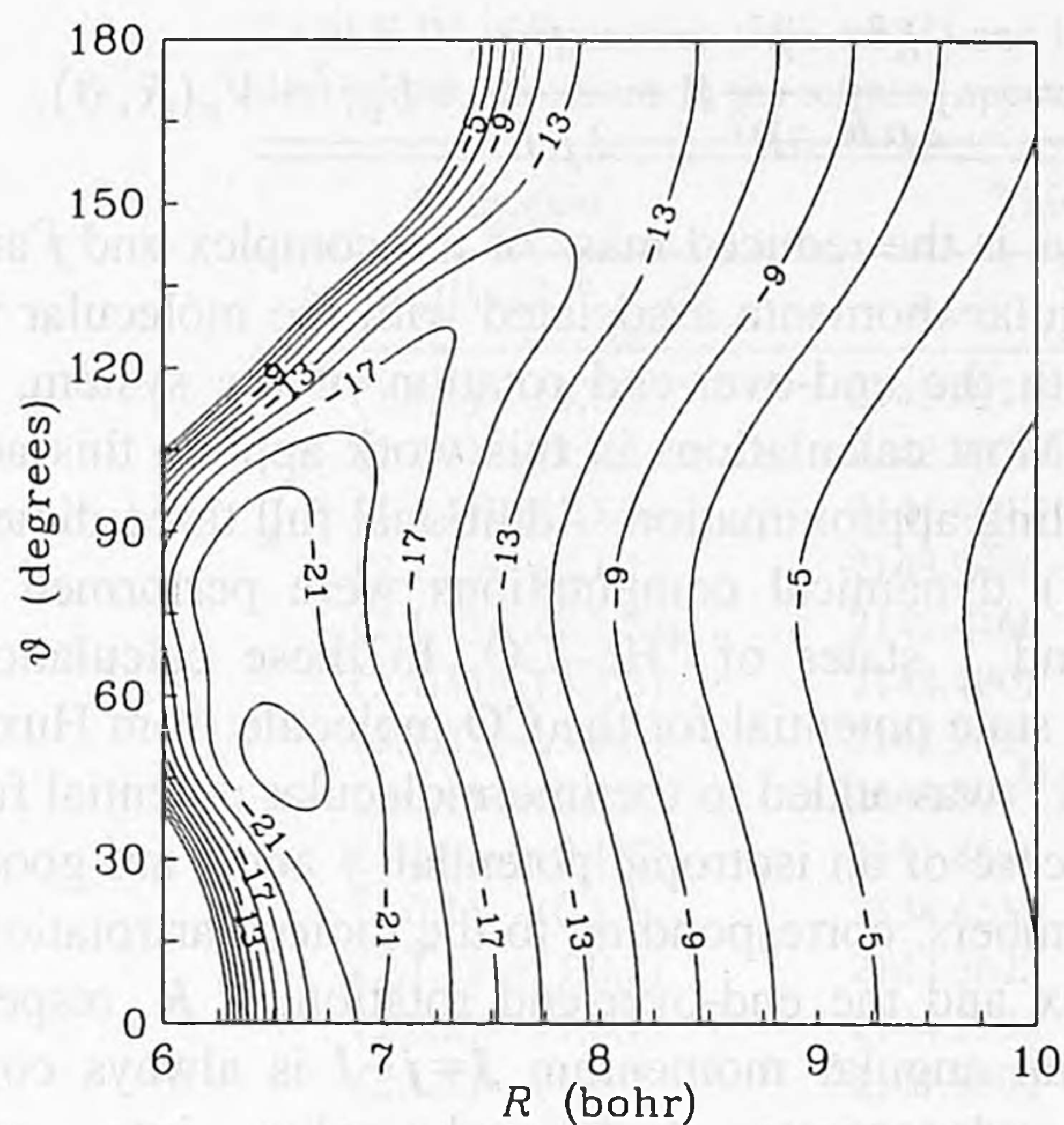


FIG. 1. Contour plot of the *ab initio* potential (in cm^{-1}) at $r = 2.132$ bohr.

most 0.5 cm^{-1} . A FORTRAN subroutine for generating the *ab initio* potential is available from the authors at the electronic mail address avda@theochem.kun.nl.

III. FEATURES OF THE POTENTIAL ENERGY SURFACE

We first look at the potential energy surface, fitted to the *ab initio* calculated data points, for r fixed at the experimental CO equilibrium bond length $r_e = 2.132$ bohr. The potential surface shows a single minimum of depth $\epsilon_m = -23.734 \text{ cm}^{-1}$ at $R_m = 6.53$ bohr and $\vartheta_m = 48.4^\circ$. Comparison with the previously published two-dimensional potential energy surface⁵ shows that the current potential predicts a minimum corresponding to the skew symmetry of the complex instead of the linear CO-He configuration. As the potential is very flat in region $\vartheta = 0^\circ$ to 120° , small inaccuracies in the basis set or the fit can cause the global minimum to shift from one geometry to the other. For the $\vartheta = 0^\circ$ curve at $r = 2.132$ bohr, the potential shows a minimal value at $R = 6.94$ bohr of $\epsilon = -21.078 \text{ cm}^{-1}$, which is only a few wave numbers above the global minimum. The improvement of the basis set, compared to Ref. 5, has a significant effect on the interaction energies. Two recently computed MBPT4 potentials predict global minima of $\epsilon = -20.32 \text{ cm}^{-1}$ at $\vartheta_m = 60^\circ$, $R_m = 6.60$ bohr,⁴ and $\epsilon_m = -21.95 \text{ cm}^{-1}$ at $\vartheta_m = 70^\circ$, $R_m = 6.43$, bohr³ i.e., at the skew geometry. By contrast, a linear equilibrium geometry with $\epsilon_m = -22.531 \text{ cm}^{-1}$, $R_m = 6.84$ bohr was predicted by the "XC" model potential,⁸ which was fitted to the infrared spectrum and was based on an exchange-Coulomb model. How difficult it is to locate the global minimum is illustrated by the fact that the older $V_{(3,3,3)}$ potential fitted to the same spectroscopic data has its minimum at the skew geometry.⁶ These *ab initio* and semi-empirical potential surfaces were compared in a recent work by Thachuk *et al.*,⁹ together with our two-dimensional potential. Agreement between the current potential and the semi-empirical XC potential, which has proved to be very accu-

TABLE I. Components of the interaction energy at $R = 7$ bohr, $r = 2.132$ bohr computed in a basis with $[8s5p3d1f]$ functions on C and O and additional bond functions for $E_{\text{disp}}^{(2)}$ (A) and a basis with $[9s7p3d2f]$ functions on C and O and no bond functions (B).

	$\vartheta = 0^\circ$		$\vartheta = 180^\circ$	
	basis A	basis B	basis A	basis B
$E_{\text{int}}^{\text{HF}}$	12.15	12.21	124.78	124.41
$\epsilon_{\text{pol}}^{(1)}$	-0.55	-0.55	-2.26	-1.85
$\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})$	5.12	5.28	8.26	6.10
$E_{\text{disp}}^{(2)}$	-38.96	-37.70	-100.65	-94.92
$E_{\text{exch-disp}}^{(2)}$	0.82	0.82	5.85	5.80
$E_{\text{int}}^{(2)}$	-21.42	-19.94	35.98	39.54

rate, is better than for our old potential surface and is now within 2 cm^{-1} . Figure 1 depicts a contour plot of the *ab initio* potential at $r = 2.132$ bohr.

In Table I we compare the separate components of the interaction energy computed in two different basis sets. In case A, all components were computed with the basis sets from Diercksen and Sadlej²⁵ for the C and O atoms, except for the contribution $E_{\text{disp}}^{(20)}$ which was calculated in the basis set with additional bond functions. The basis sets from Hettema *et al.*²⁷ for C and O were used in case B, where no bond functions were included (cf., Sec. II). From Table I it is seen that the differences between the two basis sets are manifest in two components, namely, the intramolecular correlation correction to the first-order exchange energy, $\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})$, and the dispersion energy $E_{\text{disp}}^{(2)}$. Since basis B contains more s and p functions on the CO monomer, the intramolecular correlation is taken into account to a greater extent than in basis A. It is known that molecules with triple bonds are sensitive to electronic correlation in higher-order levels of perturbation theory.³¹ This explains the difference in $\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})$, which is as large as 26% for $\vartheta = 180^\circ$. In comparison with the results from Ref. 5 we observe that at $\vartheta = 0^\circ$ and 180° the Hartree-Fock interaction energies are 0.83 and 6.50 cm^{-1} higher, respectively, while $\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})$ at $\vartheta = 0^\circ$ is 1.50 cm^{-1} higher. These deviations are caused by the incorrect contraction of the steepest p functions in Ref. 5. Second, in basis A, which includes bond functions in the calculation of $E_{\text{disp}}^{(20)}$, the dispersion energy $E_{\text{disp}}^{(2)}$ is 1.3 and 5.7 cm^{-1} lower at $\vartheta = 0^\circ$ and 180° , respectively, in comparison with basis B (without bond functions). The results for basis B are approximately equal to the results found for $E_{\text{disp}}^{(2)}$ in Ref. 5: -38.81 and -94.48 cm^{-1} at $\vartheta = 0^\circ$ and 180° , respectively. Although the calculation of $E_{\text{disp}}^{(20)}$ is not strictly variational, it follows in practice

TABLE II. Expectation values in atomic units of $(r - r_e)^k$, $k = 1, 2, 3$, for the $v = 0$ and $v = 1$ vibrational states.

	$v = 0$	$v = 1$
$\langle r - r_e \rangle$	0.007 450 2	0.022 482 1
$\langle (r - r_e)^2 \rangle$	0.004 137 7	0.012 799 0
$\langle (r - r_e)^3 \rangle$	0.000 112 0	0.000 738 8

TABLE III. Energy levels (in cm^{-1}) of the $^4\text{He-CO}$ complex, relative to the $(J,j,l)=(0,0,0)$ level at -6.7879 and -6.8359 cm^{-1} (theoretical values) for $v=0$ and $v=1$, respectively. "Experimental" values are from Ref. 7.

J	(j,l)	$v=0$		$v=1$	
		This work	"Experimental"	This work	"Experimental"
0	(0,0)	0.0	0.0	0.0	0.0
	(1,1)	5.3527	5.3911	5.3087	5.3593
1	(0,1)	0.5817	0.5769	0.5813	0.5758
	(1,0)	4.0175	3.9965	3.9921	3.9631
	(1,1)	4.3079	4.2681	4.2858	4.2362
	(1,2)	6.1049	6.0961	6.0682	6.0694
2	(0,2)	1.7333	1.7176	1.7321	1.7156
	(1,1)	4.7494	4.7345	4.7208	4.7010
	(1,2)	5.4975	5.4470	5.4748	5.4142
3	(0,3)	3.4283	3.3950	3.4264	3.3912
	(1,2)	5.9541	5.9342	5.9237	5.8996
	(1,3)	7.2441	7.1765	7.2209	7.1426
4	(0,4)	5.6160	5.5561	5.6142	5.5505
	(1,4)	9.4878	9.3940	9.4648	9.3600

that an improvement of the basis implies a lowering of $E_{\text{disp}}^{(20)}$. If only nucleus-centered basis sets are used, functions with high angular momenta have to be included to describe the dispersion energy properly. This can be avoided by extending the basis set with a series of diffuse bond functions with low angular quantum numbers. The exact origin and exponents of the bond functions hardly affect the energy. As $E_{\text{disp}}^{(20)}$ constitutes the main contribution to the dispersion energy, calculating this term (at relatively low cost) in a basis with diffuse bond functions causes the dispersion energy and consequently the total interaction energy to be substantially lowered.

IV. BOUND STATES AND INFRARED SPECTRUM OF He-CO

As is well known, nuclear motions of weakly bound van der Waals complexes can be described in a set of coordinates relative to either a space-fixed or a dimer-embedded frame.³² When the strength of the anisotropy in the intermolecular potential is small in comparison with the end-over-end rotational constant $1/(2\mu R^2)$ of the dimer, it is convenient to use the space-fixed coordinate system. It is this description that is used here even though the anisotropy of the potential in the van der Waals region is not particularly weak. We did this because the energy levels and infrared transitions of the He-CO complex can be approximately classified by the case (a) coupling of Bratoz and Martin³³ (see Refs. 32 and 34 for a review). Furthermore, the intramolecular vibration can to a good approximation be decoupled from the intermolecular modes because of the high frequency ($\sim 2143 \text{ cm}^{-1}$) of the former. The r -dependent rotational constant of CO and potential function can then be replaced by their vibrationally averaged counterparts, b_v and $V_v(R, \vartheta)$, respectively, with v labeling the intramolecular vibrational mode. The nuclear motions of He-CO are thus described by the Hamiltonian

$$H_v = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{l^2}{2\mu R^2} + b_v j^2 + V_v(R, \vartheta), \quad (3)$$

where μ is the reduced mass of the complex and j and l are the angular momenta associated with the molecular rotation and with the end-over-end rotation of the system, respectively. Most calculations in this work applied this adiabatic decoupling approximation. Additional full three-dimensional (R, ϑ, r) dynamical computations were performed for the $J=0$ and 1 states of $^4\text{He-CO}$. In these calculations, the ground state potential for the CO molecule from Huxley and Murrell³⁵ was added to the intermolecular potential function.

In case of an isotropic potential, j and l are good quantum numbers, corresponding to the molecular rotation in the complex and the end-over-end rotation of R , respectively. The total angular momentum $J=j+l$ is always conserved but a degenerate (j,l) -level splits into sublevels $J=|j-l|, \dots, j+l$ under the influence of the anisotropy of the potential. It was shown in our previous paper⁵ that for most of the eigenstates, the dominant (j,l) contribution to the wave function is of the order of 90%, suggesting that the CO molecule in the dimer behaves like a slightly hindered rotor. This was confirmed by the observation that although most transitions did not obey selection rules corresponding to the case (a) coupling of Bratoz and Martin,³³ the most intense lines did correspond to the free internal rotor limit. Therefore, the states can to be labeled a good approximation by j and l .

When we assume that the CO vibration is decoupled from the intermolecular modes, the transition frequencies are given by

$$\begin{aligned} \nu(v=1, j', l', J' \leftarrow v=0, j'', l'', J'') \\ = E_{j', l', v=1}^{J'} - E_{j'', l'', v=0}^{J''} + Q_1(0), \end{aligned} \quad (4)$$

where $Q_1(0) = 2143.2712 \text{ cm}^{-1}$ is the frequency of the CO fundamental stretching mode, determined from a Dunham analysis.³⁶ The intensities of the infrared transitions in He-CO accompanying the fundamental band of CO were calculated as in Ref. 5, at a temperature of $T=50 \text{ K}$. The intermolecular transitions obey the following selection rules: $|\Delta p|=1$ with $(-1)^p \equiv (-1)^{j+l}$, and $|\Delta J|=0$ or 1. In addition, the selection rules $\Delta l=0$ and $|\Delta j|=1$ hold approximately since j and l are nearly good quantum numbers.

To compute the vibrationally averaged potential surface $V_v(R, \vartheta)$ for a given vibrational state v of the CO monomer, the powers $(r-r_e)^k$ in the analytical expression of the potential energy were replaced by their corresponding expectation values. We have determined the eigenfunctions of the potential from Ref. 35 by using the discrete variable representation (DVR) method with a basis of sinc functions.³⁷ The expectation values of the powers of $(r-r_e)$ over the $v=0$ and $v=1$ vibrational states that were obtained from these eigenfunctions are listed in Table II.

A radial basis of Morse type oscillator functions³⁸ was used for the R coordinate. The parameters R_e , D_e , and ω_e were optimized by minimizing the energy of the $J=0$ state. This gave $R_e=13.050$ and 14.149 bohr for $^4\text{He-CO}$ and

TABLE IV. Frequencies ν (in cm^{-1}) and intensities (in arbitrary units, relative to the (3,1,2) \leftarrow (2,0,2) intensity) of the transitions in the infrared spectrum of $^4\text{He-CO}$ accompanying the fundamental band of CO.

Transition (J', j', l') \leftarrow (J'', j'', l'')	This work		Observed, Ref. 6		
	ν_{calc}	Intensity	ν_{obs}	Intensity	$\nu_{\text{calc}} - \nu_{\text{obs}}$
(1,1,1) \leftarrow (1,1,0)	2143.4916	3.3	2143.4861	3	0.005
(1,1,0) \leftarrow (1,1,1)	2142.9074	3.4	2142.9420	3	-0.035
(1,1,1) \leftarrow (1,1,2)	2141.4042	0.3	2141.3865	4	0.018
(2,1,2) \leftarrow (2,1,1)	2143.9486	4.6	2143.9265	6	0.022
(2,1,1) \leftarrow (2,1,2)	2142.4466	4.6	2142.5002	5	-0.054
(3,1,3) \leftarrow (3,1,2)	2144.4901	6.6	2144.4557	9	0.034
(3,1,2) \leftarrow (3,1,3)	2141.9029	6.6	2141.9698	6	-0.067
(1,0,1) \leftarrow (0,0,0)	2143.8045	5.8	2143.8227	8	-0.018
(1,1,0) \leftarrow (0,1,1)	2141.8626	2.3	2141.8185	3	0.044
(1,0,1) \leftarrow (0,1,1)	2138.4518	9.8	2138.4315	11	0.020
(2,1,1) \leftarrow (1,0,1)	2147.3623	74.7	2147.3709	86	-0.009
(2,0,2) \leftarrow (1,0,1)	2144.3736	11.4	2144.3852	16	-0.012
(2,1,1) \leftarrow (1,1,2)	2141.8392	6.3	2141.8516	7	-0.012
(2,0,2) \leftarrow (1,1,0)	2140.9378	4.4	2140.9656	6	-0.028
(2,0,2) \leftarrow (1,1,2)	2138.8505	28.7	2138.8665	31	-0.016
(3,1,2) \leftarrow (2,0,2)	2147.4137	100.0	2147.4290	100	-0.015
(3,0,3) \leftarrow (2,0,2)	2144.9163	16.5	2144.9202	20	-0.004
(3,0,3) \leftarrow (2,1,1)	2141.9002	4.5	2141.9031	5	-0.003
(4,0,4) \leftarrow (3,0,3)	2145.4091	19.6	2145.4024	25	0.007
(4,0,4) \leftarrow (3,1,2)	2142.8834	3.4	2142.8628	3	0.021
(0,1,1) \leftarrow (1,0,1)	2147.9502	11.3	2148.0289	13	-0.079
(0,1,1) \leftarrow (1,1,0)	2144.5144	2.4	2144.6096	2	-0.095
(0,0,0) \leftarrow (1,0,1)	2142.6416	5.7	2142.6698	6	-0.028
(1,1,2) \leftarrow (2,0,2)	2147.5582	33.0	2147.5983	36	-0.040
(1,1,0) \leftarrow (2,0,2)	2145.4820	4.7	2145.4924	6	-0.010
(1,1,2) \leftarrow (2,1,1)	2144.5421	6.6	2144.5818	6	-0.040
(1,0,1) \leftarrow (2,0,2)	2142.0712	10.9	2142.1049	14	-0.034
(1,0,1) \leftarrow (2,1,1)	2139.0551	66.0	2139.0877	86	-0.033
(2,1,1) \leftarrow (3,0,3)	2144.5157	4.6	2144.5531	5	-0.037
(2,0,2) \leftarrow (3,1,2)	2139.0013	88.3	2139.0281	94	-0.027
(3,1,2) \leftarrow (4,0,4)	2143.5310	3.4	2143.5898	5	-0.059
(3,0,3) \leftarrow (4,0,4)	2141.0336	17.8	2141.0822	23	-0.049

Hidden lines

Transition (J', j', l') \leftarrow (J'', j'', l'')	This work		Observed, Ref. 7	
	ν_{calc}	Intensity	ν_{obs}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
(0,0,0) \leftarrow (1,1,0)	2139.2057	40.8	2139.2502	-0.044
(4,0,4) \leftarrow (4,1,4)	2139.3496	115.0	2139.4032	-0.054
(3,0,3) \leftarrow (3,1,3)	2139.4055	97.1	2139.4613	-0.056
(2,0,2) \leftarrow (2,1,2)	2139.4579	74.2	2139.5154	-0.058
(1,0,1) \leftarrow (1,1,1)	2139.4966	46.6	2139.5543	-0.058
(1,1,1) \leftarrow (1,0,1)	2146.9274	52.2	2146.9061	0.021
(2,1,2) \leftarrow (2,0,2)	2146.9648	83.3	2146.9433	0.022
(3,1,3) \leftarrow (3,0,3)	2147.0158	109.2	2146.9943	0.022
(4,1,4) \leftarrow (4,0,4)	2147.0720	129.8	2147.0506	0.021
(1,1,0) \leftarrow (0,0,0)	2147.2153	46.1	2147.2098	0.006

$^3\text{He-CO}$, respectively, $D_e = 14.3758 \text{ cm}^{-1}$, and $\omega_e = 9.9861 \text{ cm}^{-1}$. The final basis was restricted to the space with $j \leq 10$ for the angular basis and order $n \leq 23$ for the radial basis. The vibrationally averaged rotational constants b_0 and b_1 of the CO molecule were fixed at $1.922 5125$ and $1.905 0074 \text{ cm}^{-1}$, respectively.³⁹ The rotational constant for the vibrational ground state is close to the highly accurate value of $1.922 528 988 \text{ cm}^{-1}$ reported by Varberg and Evenson.⁴⁰ In the full three-dimensional calculations a Morse type basis for r was used with $r_e = 2.1597$ bohr, $D_e^r = 82 303.0 \text{ cm}^{-1}$, $\omega_e^r = 2142.95 \text{ cm}^{-1}$, and order $n \leq 4$. We used the following

masses:⁴¹ ^3He —3.01603 amu, ^4He —4.002 60 amu, ^{12}C —12 amu, and ^{16}O —15.994 91 amu. For practical reasons, all calculations were performed by the TRIATOM package,⁴² which uses the dimer-embedded frame, rather than by the ATDIATSF package,⁴³ which is based on a space-fixed coordinate system. Note that both descriptions give exactly the same results, only the approximate quantum numbers labeling the states are different.

In Table III we summarize the results of the bound state calculations for $^4\text{He-CO}$. There are 14 bound states, which can be labeled approximately by angular momentum quan-

TABLE V. Energy levels (in cm^{-1}) of the $^3\text{He-CO}$ complex, relative to the $(J,j,l)=(0,0,0)$ level at -5.5416 and -5.5858 cm^{-1} (theoretical values) for $v=0$ and $v=1$, respectively. "Experimental" values are from Ref. 7.

J	(j,l)	$v=0$		$v=1$	
		This work	"Experimental"	This work	"Experimental"
0	(0,0)	0.0	0.0	0.0	0.0
	(1,1)	5.2131	5.1800	5.1781	5.1629
1	(0,1)	0.7069	0.7022	0.7066	0.7002
	(1,0)	3.9915	3.9771	3.9640	3.9404
	(1,1)	4.4226	4.3869	4.3990	4.3517
2	(0,2)	2.0968	2.0766	2.0961	2.0721
	(1,1)	4.8145	4.8031	4.7846	4.7673
	(1,2)	5.8609	5.8087	5.8371	5.7744
3	(0,3)	4.1108	4.0626	4.1106	4.0590
	(1,3)	7.9367	— ^a	7.9133	7.8232

^aThis level has not been directly observed; it is estimated to be at 7.856 cm^{-1} .

tum numbers j and l . The potential energy surface does not support states excited in the van der Waals stretch. It should be noted that states of positive energy lying below the $j=1$ rotational level of the CO monomer are truly bound if they have parity $p=(-1)^{j+1}$. These states cannot mix with $j=0$ continuum states, which have parity $p=(-1)^j$, since both p and J are conserved. The $j=1$ rotational level of CO in its ground state was experimentally determined at 3.8450 cm^{-1} .⁴⁰ The ground state of $^4\text{He-CO}$ is bound by 6.788 cm^{-1} . Our earlier two-dimensional SAPT potential⁵ supports

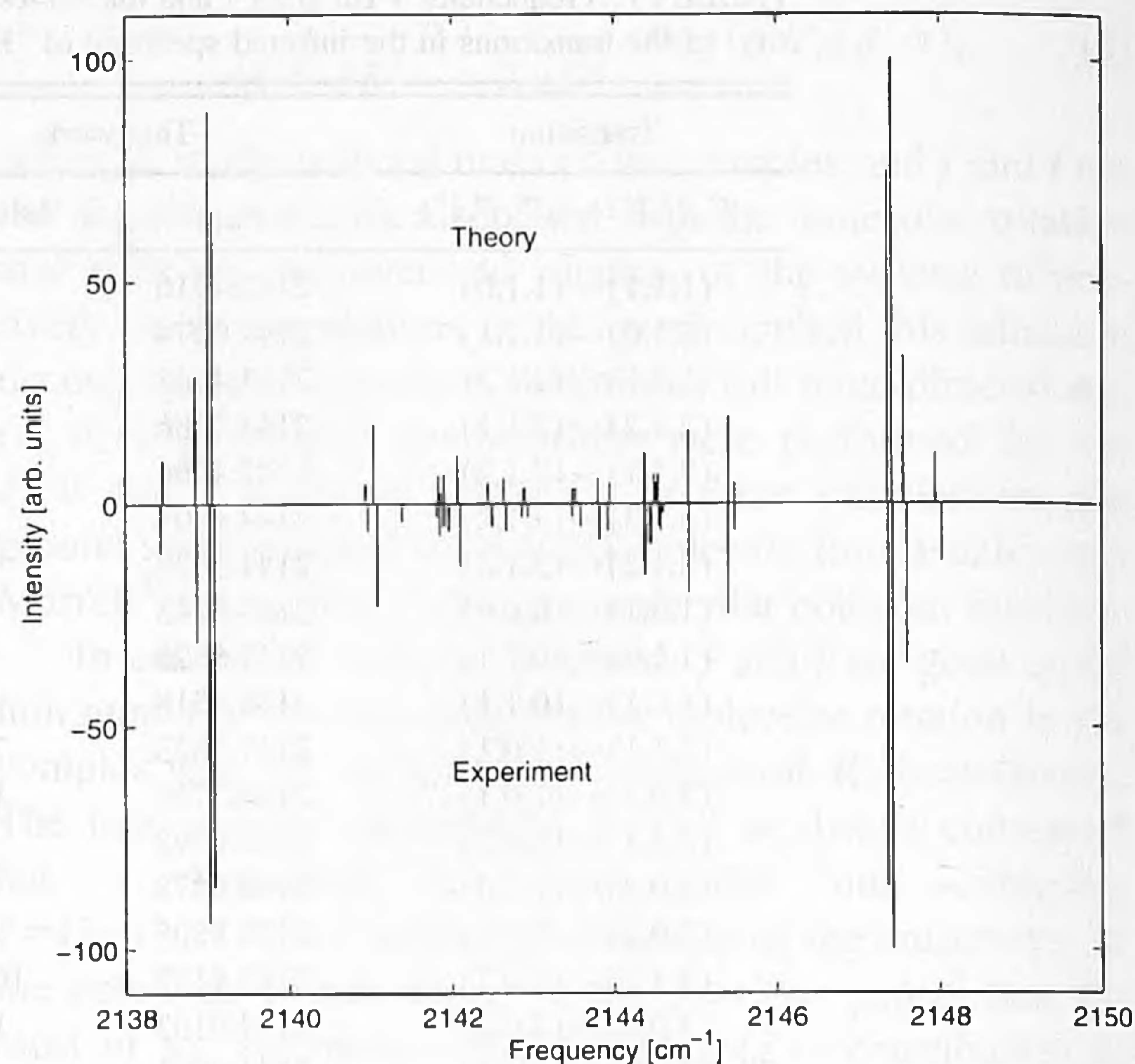


FIG. 2. Comparison of theoretical and experimental infrared spectra of the $^4\text{He-CO}$ complex accompanying the fundamental band of CO. The temperature is 50 K.

a ground state lying 0.174 cm^{-1} lower, which is in agreement with the observation that the old potential has a slightly deeper well. The "experimental" energy level scheme

TABLE VI. Frequencies ν (in cm^{-1}) and intensities (in arbitrary units, relative to the $(2,1,1) \leftarrow (1,0,1)$ intensity) of the transitions in the infrared spectrum of $^3\text{He-CO}$ accompanying the fundamental band of CO.

Transition $(J',j',l') \leftarrow (J'',j'',l'')$	This work		Observed, Ref. 6		
	ν_{calc}	Intensity	ν_{obs}	Intensity	$\nu_{\text{calc}} - \nu_{\text{obs}}$
(1,0,1) \leftarrow (0,0,0)	2143.9335	6.3	2143.9489	9	-0.015
(1,0,1) \leftarrow (0,1,1)	2138.7204	12.7	2138.7701	8	-0.050
(2,1,1) \leftarrow (1,0,1)	2147.3047	100.0	2147.3152	100	-0.010
(2,0,2) \leftarrow (1,0,1)	2144.6162	12.4	2144.6192	11	-0.003
(3,0,3) \leftarrow (2,0,2)	2145.2407	17.0	2145.2323	15	0.008
(0,1,1) \leftarrow (1,0,1)	2147.6981	14.8	2147.7105	8	-0.012
(0,0,0) \leftarrow (1,0,1)	2142.5201	6.1	2142.5489	6	-0.029
(1,0,1) \leftarrow (2,0,2)	2141.8367	11.7	2141.8728	11	-0.036
(1,0,1) \leftarrow (2,1,1)	2139.1190	88.5	2139.1471	95	-0.028
(2,0,2) \leftarrow (3,0,3)	2141.2123	15.6	2141.2593	15	-0.047
(2,1,2) \leftarrow (2,1,1)	2144.2495	5.3	2144.2203	5	0.029
(2,1,1) \leftarrow (2,1,2)	2142.1507	5.4	2142.2080	6	-0.057
Hidden lines					
Transition $(J',j',l') \leftarrow (J'',j'',l'')$	This work		Observed, Ref. 7		
	ν_{calc}	Intensity	ν_{obs}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	
(0,0,0) \leftarrow (1,1,0)	2139.2354	55.3	2139.2728	-0.037	
(3,0,3) \leftarrow (3,1,3)	2139.4009	124.5	— ^a	—	
(2,0,2) \leftarrow (2,1,2)	2139.4622	96.1	2139.5133	-0.051	
(1,0,1) \leftarrow (1,1,1)	2139.5110	61.0	2139.5633	-0.052	
(1,1,1) \leftarrow (1,0,1)	2146.9191	68.3	2146.8994	0.020	
(2,1,2) \leftarrow (2,0,2)	2146.9672	107.9	2146.9478	0.019	
(3,1,3) \leftarrow (3,0,3)	2147.0295	140.1	2147.0105	0.019	
(1,1,0) \leftarrow (0,0,0)	2147.1910	62.3	2147.1903	0.001	

^aThis line has not been observed.

shown in Table III was reported by Chan and McKellar⁷ who slightly modified the levels from Chuaqui *et al.*⁶ by including the transition frequencies of the hidden lines. Furthermore, their scheme includes the $(J, j, l) = (4, 1, 4)$ level.

Full three-dimensional calculations for $^4\text{He-CO}$ ($J=0$ and 1) showed that the bound levels are affected by less than 0.001 cm^{-1} by the decoupling approximation. For instance, the $(J, j, l) = (1, 1, 1)$ state for $v=0$ is decreased from 4.3083 to 4.3079 cm^{-1} by this approximation, while the $(J, j, l) = (0, 1, 1)$ state for $v=1$ is increased from 5.3086 to 5.3087 cm^{-1} . This is in agreement with the result found for the He-HF complex³⁸ that the coupling between inter- and intramolecular modes is very small for atom-diatom systems.

The calculated infrared transition frequencies and intensities for the $^4\text{He-CO}$ complex are reported in Table IV and graphically illustrated in Fig. 2. Table IV shows that the agreement of theoretical transition frequencies with the results of the high-resolution measurements^{6,7} is excellent. All line positions agree within 0.1 cm^{-1} or better, while the rms. deviation is 0.038 cm^{-1} . The absolute errors of the transition frequencies computed from our previous two-dimensional *ab initio* potential⁵ were as large as 0.5 cm^{-1} for some transitions. Only after scaling the short-range contribution to the $V_2(R)$ component of the potential energy agreement within 0.2 cm^{-1} for all transitions was reached, whereas the agreement we obtain now is twice as good without any scaling. The transition intensities predicted by the *ab initio* potential also agree reasonably well with the experimental values. One should keep in mind that intensities are determined from experiment with much less accuracy than the corresponding transition frequencies.⁶

In Table V we report the bound state levels for the $^3\text{He-CO}$ complex generated from the *ab initio* potential. The 12 transitions observed in Ref. 6 for $^3\text{He-CO}$ were insufficient to determine the energy levels accurately. The addition of seven new transitions, however, enabled the authors of Ref. 7 to construct the experimental energy level scheme listed in Table V. The experimental $(J, j, l) = (3, 1, 3)$ level is absent since the $(3, 0, 3) \leftarrow (3, 1, 3)$ transition could not be observed. Table VI and Fig. 3 show the *ab initio* transition frequencies and intensities for the $^3\text{He-CO}$ complex, together with their experimental counterparts from Refs. 6 and 7. Agreement with experiment is equally good as for $^4\text{He-CO}$. All line positions are reproduced within 0.06 cm^{-1} ; the rms. deviation is 0.033 cm^{-1} . The infrared intensities are also correctly predicted. The excellent agreement between theoretical and experimental transition frequencies for both $^4\text{He-CO}$ and $^3\text{He-CO}$ confirms that the *ab initio* calculated potential energy surface represents the anisotropy of the potential in the region of the van der Waals minimum very accurately.

The band origin of the $v=1 \leftarrow 0$ transition is lower in the He-CO complex than in the free monomer. The observed red shifts for $^4\text{He-CO}$ and $^3\text{He-CO}$ are -0.024 and -0.021 cm^{-1} , respectively,⁷ the theoretical values are -0.048 and -0.044 cm^{-1} , respectively. This overestimation of the red shifts is reflected in the mean difference between

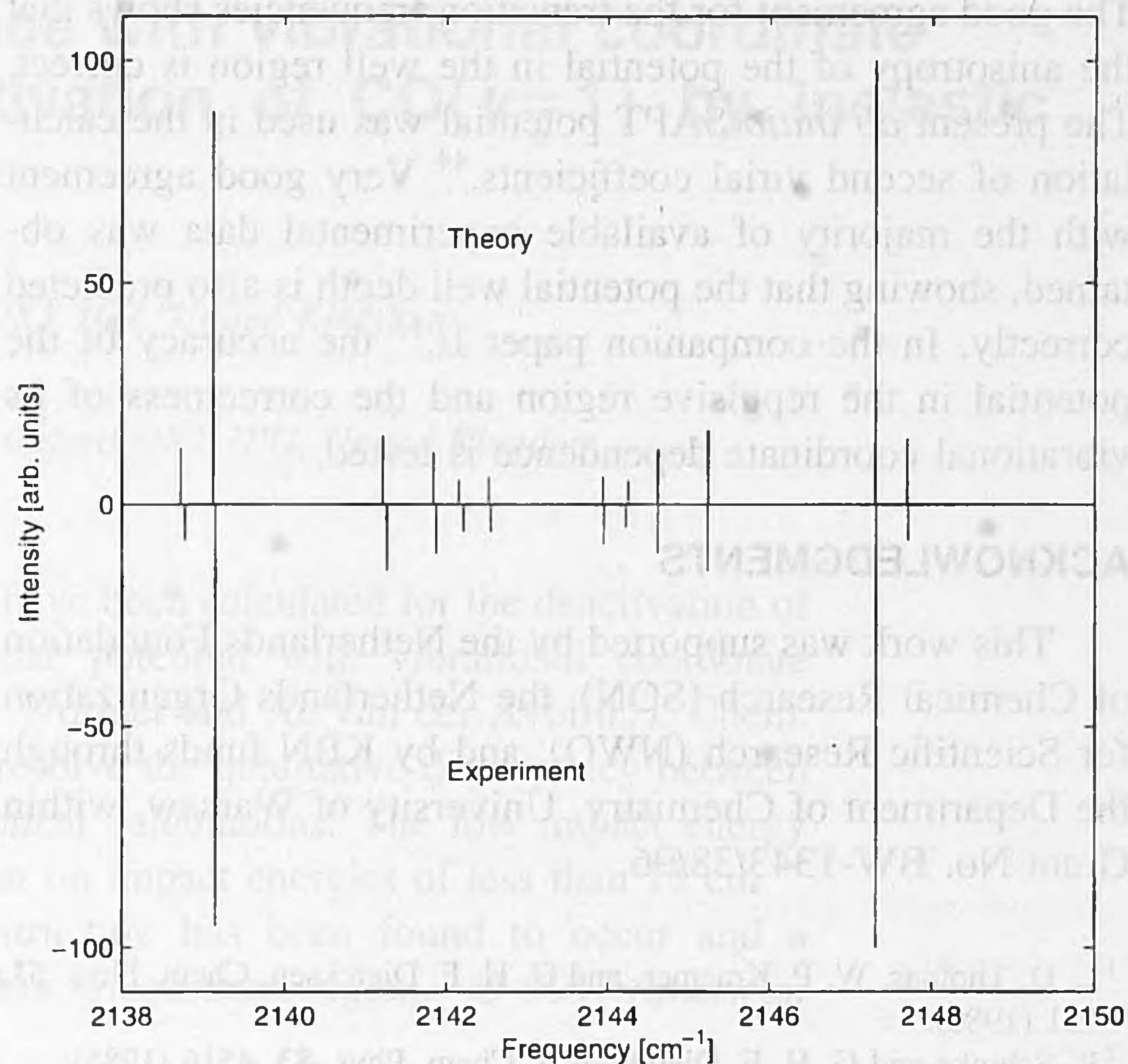


FIG. 3. Comparison of theoretical and experimental infrared spectra of the $^3\text{He-CO}$ complex accompanying the fundamental band of CO. The temperature is 50 K.

calculated and observed transition frequencies which are -0.019 and -0.017 cm^{-1} , respectively. As discussed above, the bound state levels obtained from three-dimensional and decoupled two-dimensional calculations agree within 0.001 cm^{-1} . The same result was found for the band origin. Therefore, we conclude that the remaining small disagreements between theoretical and experimental red shifts must be due to minor inaccuracies in the potential function, rather than to the decoupling approximation.

V. SUMMARY AND CONCLUSIONS

The interaction potential energy surface of the He-CO complex was calculated for a broad range of configurations using symmetry-adapted perturbation theory. In comparison with previous work⁵ the anisotropy of the exchange-repulsion energy was computed by the more advanced SAPT-CCSD method, the basis set was improved, and the CO bond length was varied over five values, which yields a full three-dimensional potential surface. We have shown that the present potential agrees very well with the accurate semi-empirical XC potential of Le Roy *et al.*,⁸ better than our earlier *ab initio* potential.

Using the computed potential energy surface we have calculated bound rovibrational states and the infrared spectrum of the He-CO complex corresponding to the simultaneous excitation of the vibration and hindered rotation of the CO molecule within the dimer. Variational characterization of the rovibrational states revealed a ground state of $^4\text{He-CO}$ with a dissociation energy of 6.79 cm^{-1} and several angularly excited states of the complex. The predicted positions and intensities of lines in the infrared spectrum are in excellent agreement with the experimental spectrum.^{6,7}

The good agreement for the transition frequencies shows that the anisotropy of the potential in the well region is correct. The present *ab initio* SAPT potential was used in the calculation of second virial coefficients.⁴⁴ Very good agreement with the majority of available experimental data was obtained, showing that the potential well depth is also predicted correctly. In the companion paper II,¹³ the accuracy of the potential in the repulsive region and the correctness of its vibrational coordinate dependence is tested.

ACKNOWLEDGMENTS

This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and by KBN funds through the Department of Chemistry, University of Warsaw, within Grant No. BW-1343/38/96.

- ¹L. D. Thomas, W. P. Kraemer, and G. H. F. Diercksen, *Chem. Phys.* **51**, 131 (1980).
- ²R. Schinke and G. H. F. Diercksen, *J. Chem. Phys.* **83**, 4516 (1985).
- ³B. Kukawska-Tarnawska, G. Chalasinski, and K. Olszewski, *J. Chem. Phys.* **101**, 4964 (1994).
- ⁴F. M. Tao, S. Drucker, R. C. Cohen, and W. Klemperer, *J. Chem. Phys.* **101**, 8680 (1994).
- ⁵R. Moszynski, T. Korona, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **103**, 321 (1995).
- ⁶C. E. Chuaqui, R. J. Le Roy, and A. R. W. McKellar, *J. Chem. Phys.* **101**, 39 (1994).
- ⁷M. C. Chan and A. R. W. McKellar, *J. Chem. Phys.* **105**, 7910 (1996).
- ⁸R. J. Le Roy, C. Bissonnette, T. H. Wu, A. K. Dham, and W. J. Meath, *Faraday Discuss.* **97**, 81 (1994).
- ⁹M. Thachuk, C. E. Chuaqui, and R. J. Le Roy, *J. Chem. Phys.* **105**, 4005 (1996).
- ¹⁰M. M. Beaky, T. M. Goyette, and F. C. De Lucia, *J. Chem. Phys.* **105**, 3994 (1996).
- ¹¹A. K. Dham and W. J. Meath, *Mol. Phys.* **88**, 339 (1996).
- ¹²E. L. Heck and A. S. Dickinson, *Mol. Phys.* **91**, 31 (1997).
- ¹³J. P. Reid, H. M. Quiney, and C. J. S. M. Simpson, *J. Chem. Phys.* **107**, 9929 (1997).
- ¹⁴R. Moszynski, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **102**, 8385 (1995).
- ¹⁵R. Moszynski, T. Korona, P. E. S. Wormer, and A. van der Avoird, *J. Phys. Chem. A* **101**, 4690 (1997).
- ¹⁶T. G. A. Heijmen, T. Korona, R. Moszynski, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **107**, 902 (1997).
- ¹⁷M. Jeziorska, B. Jeziorski, and J. Cizek, *Int. J. Quantum Chem.* **32**, 149 (1987).
- ¹⁸R. Moszynski, T. G. A. Heijmen, and B. Jeziorski, *Mol. Phys.* **88**, 741 (1996).
- ¹⁹A. J. Sadlej, *Mol. Phys.* **39**, 1249 (1980).
- ²⁰M. Jaszunski, *Mol. Phys.* **39**, 777 (1980).
- ²¹G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- ²²G. Herzberg, *Molecular Spectra and Molecular Structure, Vol 1: Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
- ²³F. B. van Duijneveldt, IBM Research Report, RJ945 (1971).
- ²⁴M. Gutowski, J. Verbeek, J. H. van Lenthe, and G. Chalasinski, *Chem. Phys.* **111**, 396 (1987).
- ²⁵G. H. F. Diercksen and A. J. Sadlej, *Chem. Phys.* **96**, 17 (1985); *ibid.*, **43** (1985).
- ²⁶F. M. Tao and Y. K. Pan, *J. Chem. Phys.* **97**, 4989 (1992).
- ²⁷H. Hettema, P. E. S. Wormer, and A. J. Thakkar, *Mol. Phys.* **80**, 533 (1993).
- ²⁸B. Jeziorski, R. Moszynski, A. Ratkiewicz, S. Rybak, K. Szalewicz, and H.L. Williams, "SAPT: A Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interactions," in *Methods and Techniques in Computational Chemistry: METECC-94, vol. B Medium Size Systems*, edited by E. Clementi (STEF, Cagliari, 1993), p. 79.
- ²⁹P. E. S. Wormer and H. Hettema, *J. Chem. Phys.* **97**, 5592 (1992); P. E. S. Wormer and H. Hettema, POLCOR package (Nijmegen 1992).
- ³⁰S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ³¹C. M. van Heusden, R. Kobayashi, R. G. Amos, and N. C. Handy, *Theor. Chim. Acta* **86**, 25 (1993).
- ³²A. van der Avoird, P. E. S. Wormer, and R. Moszynski, *Chem. Rev.* **94**, 1931 (1994).
- ³³S. Bratoz and M. L. Martin, *J. Chem. Phys.* **42**, 1051 (1965).
- ³⁴J. M. Hutson, *Adv. Mol. Vib. Collision Dyn.* **1**, 1 (1991).
- ³⁵Ph. Huxley and J. N. Murrell, *J. Chem. Soc. Faraday Trans. II* **79**, 323 (1983).
- ³⁶A. G. Maki, J. S. Wells, and D. A. Jennings, *J. Mol. Spectrosc.* **144**, 224 (1990).
- ³⁷G. C. Groenenboom and D. T. Colbert, *J. Chem. Phys.* **99**, 9681 (1993).
- ³⁸J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.* **79**, 43 (1983).
- ³⁹A. W. Mantz, J. K. G. Watson, K. N. Rao, D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, *J. Mol. Spectrosc.* **39**, 180 (1971).
- ⁴⁰T. D. Varberg and K. M. Evenson, *Ap. J.* **385**, 763 (1992).
- ⁴¹*Handbook of Chemistry and Physics*, edited by R.C. Weast and M.J. Asth (CRC, Boca Raton, 1981).
- ⁴²J. Tennyson, S. Miller, and C. R. Le Sueur, *Comput. Phys. Commun.* **75**, 339 (1993).
- ⁴³J. Tennyson, *Comput. Phys. Commun.* **29**, 307 (1983).
- ⁴⁴R. Moszynski, T. Korona, T. G. A. Heijmen, P. E. S. Wormer, A. van der Avoird, and B. Schramm, *Pol. J. Chem.* (in press).