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Potential Energy Curves for the $^1\Sigma^+$ and $^{1,3}\Pi$ States of CO[†]

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Ab initio potential energy curves of CO are calculated to address a number of problems remaining in the interpretation of the experimental VUV absorption spectra. The calculations are of the type SCF MRSD-CI. We employed the aug-cc-pVQZ basis set for both carbon and oxygen, augmented with twelve diffuse functions, of s-, p-, and d-type, located on both atomic centers. We focus on the energy region 85 000 cm^{-1} < E < 110 000 cm^{-1} characterized by strong interactions between Rydberg and valence states. In this work we deal specifically with the $^1\Sigma^+$, $^1\Pi$, and $^3\Pi$ states lying in this region. Some of the relevant findings are as follows: The minimum of the C$'^1\Sigma^+$ valence state is found 1920 cm^{-1} above the value inferred from an extrapolation of experimental data. A new $^1\Pi$ valence state, labeled E$'$, is found to perturb strongly the (X$^2\Sigma^+$)3pπ E$^1\Pi$ Rydberg state. The electrostatic perturbation of the (X$^2\Sigma^+$)3pπ c$^3\Pi$ Rydberg state by the k$^3\Pi$ valence state is confirmed. The energy position of the (A$^2\Pi$)3sσ $^3\Pi$ state, the triplet companion of the W$^1\Pi$ Rydberg state, is predicted.

Introduction

CO is the second most abundant molecule in interstellar space, only after H_2, and is thus of great relevance in astrophysics. A number of ab initio calculations have been performed on carbon monoxide but, surprisingly enough, a complete study treating together valence and Rydberg states is still lacking. A recent paper,[1] pointed out the need for new ab initio calculations of CO to assist in the unravelling and understanding of the VUV spectrum. A number of bands, mainly of $^1\Pi$ symmetry, have indeed been observed in the 10.5−14 eV energy region,[2] yet several of them are still unassigned. These bands are strongly perturbed and previous attempts[2,3] to deperturb some of them have not explained globally the general spectral features. It is clear that there are strong perturbations in the aforementioned VUV region, between Rydberg $^1\Pi$ states and one or more valence $^1\Pi$ states that have not yet been clearly identified and accounted for. In this work we provide evidence of the existence of a strong mixing between a $^1\Pi$ Rydberg state and a $^1\Pi$ valence state, i.e., between the (X$^2\Sigma^+$)3pπ E$^1\Pi$ Rydberg and the E$'^1\Pi$ valence states. This finding results from an analysis of the vibrational levels of the composite E−E$'$ adiabatic curve.

We have also computed the electrostatic mixing between the (X$^2\Sigma^+$)3pπ c$^3\Pi$ Rydberg state and the k$^3\Pi$ valence state, the triplet species associated, respectively, with the E and E$'$ singlet states; our computed value of the c−k mixing is compared with the value deduced from experiment. We also predict the energy position of the (yet unobserved) triplet state associated with the (A$^2\Pi$)3sσ W$^1\Pi$ Rydberg state. In the following section we review briefly previous calculations.

Previous ab Initio Calculations of CO

A. Valence States. The first calculation of the valence states of CO was reported by O'Neil and Schaefer in 1970.[4] These authors used Slater orbitals and carried out a configuration interaction (CI) calculation including up to 328 configurations. Their basis set did not include diffuse orbitals. However, their calculation is of interest because it is the only one representing repulsive potential curves, useful to treat predissociation problems. Another CI calculation, including up to 100 configurations and employing also a Slater basis set, was performed in 1973[5] to calculate the important spin−orbit perturbations among the valence states; the calculations employed the self-consistent field (SCF) molecular orbitals (MOs) appropriate for each of the computed valence states. The agreement with the experimental spectroscopic constants was better in this latter work than that of the previous calculations.[4] Hence, we report in Table 1 our early data[5] for the a$'^3\Sigma^+$, d$^3\Delta$, and e$^3\Sigma^-$ states and in Table 6 those of k$^3\Pi$ and c$^3\Pi$ because no new ab initio calculations have been reported on these states ever since, except however, for the a$'^3\Sigma^+$ and d$^3\Delta$ states, the work of Kirby and Liu[6] where no spectroscopic constants have been given. In 1981, Cooper and Langhoff[7] performed CI calculations that relied on Slater orbitals and included 3s and 3pσ diffuse functions on both C and O. The procedure involved matrices encompassing around 10 000 spin-adapted configuration state functions (CSFs). Some of their results are still the best for a number of states, namely,

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TABLE 1: Spectroscopic Constants of the Lowest Valence Electronic States of $^{12}C^{16}O$[a]

state	configuration	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ref
$X^1\Sigma^+$	$4\sigma^2 5\sigma^2 1\pi^4$	0.0	1.12832	2169.814	13.288	exp[13]
		0.0	1.131	2178.0	13.0	11
$a'^3\Sigma^+$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	55825.5	1.3523	1228.60	10.468	exp[13]
		55540.0	1.345	1240.0		5
$d^3\Delta$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	61120.1	1.3696	1171.94	10.635	exp[13]
		60560.0	1.373	1150.0		5
$e^3\Sigma^-$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	64230.2	1.384	1117.7	10.686	exp[13]
		62710.0	1.390	1100.0		5
$I^1\Sigma^-$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	65084.4	1.3911	1092.22	10.70	exp[13]
		65089.4	1.395	1114.7	12.1	7
$D^1\Delta$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	65928.0	1.399	1094.0	10.20	exp[13]
		65977.0	1.408	1038.0	11.9	8

[a] Column 2 gives the dominant configuration.

for $a^3\Pi$, $I^1\Sigma^-$, and $D'^1\Sigma^+$.[7] For $D^1\Delta$ the best results were obtained by Rosenkrantz and Kirby[8] using the method of Cooper and Kirby.[9]

Finally, relatively accurate multireference single- and double-excitation configuration interaction (MRD-CI) calculations[10] were performed for the singlet states by Chantranupong et al.[11] These authors used the (5s3p) contracted Gaussian basis set of Dunning[12] augmented with two additional d functions on each atom and two s and two p diffuse orbitals centered at the midpoint of the C−O bond. Their results are the best for the $X^1\Sigma^+$ ground state and the $A^1\Pi$ valence state (see Tables 1 and 5).

Very recently Varandas[14] carried out a detailed study of $A^1\Pi$ to account for the small barrier in the potential energy curve, located at about 2.25 Å. The computed height of the barrier is 594 cm^{-1} (exp: 950 ± 150 cm^{-1} ref 15).

B. Rydberg States with a $X^2\Sigma^+$ Core. The first calculation of the Rydberg states of CO was carried out by Lefebvre-Brion et al. in 1964.[16] These authors first identified the E state as a $^1\Pi$ state, rather than as a $^1\Sigma^+$ state, as previously believed. This theoretical prediction[16] was later confirmed experimentally by Tilford et al.[17] in 1965. These authors also predicted the existence of a $^3\Pi(3p\pi)$ Rydberg state at 11.4 eV. This state was later observed by Ginter and Tilford at 11.55 eV[18] and named $c^3\Pi$.

Several studies have been performed on the $^1\Sigma^+$ Rydberg states of CO (see summary in ref 1), in part due to the fact that $B^1\Sigma^+$, the first member of the $ns\sigma$ Rydberg series, exhibits strong perturbations as well as different kinds of predissociation processes. The best previous results for the $B^1\Sigma^+$ (3sσ), $C^1\Sigma^+$ (3pσ), and $E^1\Pi(3p\pi)$ Rydberg states were obtained by Chantranupong et al.[11] The absence in their calculations of the $G^1\Pi(3d\pi)$ state and the poor results obtained for the $L^1\Pi(4p\pi)$ state are probably due to the small number of Rydberg functions in their basis set. The work of Li et al.[19] which reported potential curves of the B, C, D, and D′ $^1\Sigma^+$ states aims at studying the predissociation of CO and does not report spectroscopic constants (aside ΔG_v).

Very recently Le Padellec et al.[20] published a figure depicting ab initio potential curves of a number of $^1\Sigma^+$ states of CO and $^2\Sigma^+$ states of CO$^+$. However, these authors do not report the spectroscopic constants associated with these potential curves. The purpose of their calculations was the study of the associative ionization, i.e., the reaction $C^- + O^+ \rightarrow CO^+ + e$. The atomic basis set of these authors does not contain diffuse orbitals so they did not obtain potential energy curves of Rydberg states (except for the $B^1\Sigma^+$ (3sσ) state).

For higher lying Rydberg states, only vertical excitation energies (VEE) have been reported. Table 2, column 3, gives the results of Tennyson.[21] These results were obtained by the **R**-matrix method, using Slater atomic orbitals, employing the complete active space (CAS) target states in the close-coupling expansion. Our results are reported in column 4 and the corresponding experimental values, approximated by ν_{00},[13] are given in column 5.

TABLE 2: Vertical Excitation Energies (eV) of the Rydberg States of CO at $R_e(X^1\Sigma^+)$ = 2.132 au

state	Rydberg orbital	calc ref 21	calc this work	exp[a]
$B^1\Sigma^+$	3sσ	10.84	10.82	10.78
$C^1\Sigma^+$	3pσ	11.39	11.46	11.40
$F^1\Sigma^+$	3dσ	12.34	12.55	12.4
$J^1\Sigma^+$	4sσ	12.52	12.64	12.6
$E^1\Pi$	3pπ	11.55	11.49	11.52
$G^1\Pi$	3dπ	12.45	12.50	12.5
$L^1\Pi$	4pπ	12.73	12.73	12.8
$c^3\Pi$	3pπ	11.14	11.41	11.42

[a] ν_{00} from ref 13.

C. Rydberg States with a $A^2\Pi$ Core. In 1987 Cooper and Kirby[9] carried out full-valence multiconfiguration self-consistent field (MCSCF) calculations using Slater orbitals and including diffuse orbitals on each nucleus, namely, two 3s, one 3pσ and one 3pπ functions. A reexamination of their results in 1988 led Cooper and Kirby[22] to predict the existence of a new $^1\Pi$ Rydberg state with a CO$^+$($A^2\Pi$) core and a 3sσ electron. This state seems to correspond to the observed $W^1\Pi$ state. However, since the calculated adiabatic $^1\Pi$ curve undergoes several changes of leading configuration(s) as the C−O bond length increases, it is clear that the $W^1\Pi$ Rydberg state is probably mixed with $E^1\Pi(3p\pi)$ and with (at least) one valence state. In the current work we attempt to clarify this matter.

Discussion of the $^1\Pi$ states

The valence state $A^1\Pi$ results from the $5\sigma \rightarrow 2\pi$ excitation. This state is well-known for its numerous spin−orbit perturbations which have been documented experimentally and interpreted in detail by Field (see for example ref 23). Conversely, the A state does not seem to be subject to electrostatic perturbations. The first Rydberg $^1\Pi$ state of CO is $E^1\Pi(3p\pi)$. The vibrational intervals and rotational constants of the first three vibrational levels of $E^1\Pi$ decrease at a much faster rate than do those of its $X^2\Sigma^+$ ion core.[24] The observation of the ($A^2\Pi$)3sσ $W^1\Pi$ state[13] prompted Eidelsberg and Rostas[25] to assign four successive bands, lying at longer wavelengths, to the $^3\Pi$ state with a CO$^+$ ($A^2\Pi$) core and a 3sσ Rydberg electron, that is, to the triplet companion of $W^1\Pi$.[25] However, a later study by Drabbels et al.[26] showed that these bands did not have spin structure. Consequently, Eidelsberg et al.[3] reassigned the bands to higher vibrational levels of the $E^1\Pi$ state. Eidelsberg et al.[3] carried out a deperturbation procedure including three $^1\Pi$ levels, namely, the 4p complex ($v = 0$), the $v = 1$ level of G(3dπ), and the E(3pπ) $v = 6$ level. This latter level does not appear in $^{12}C^{16}O$ but it does show up in other isotopomers. However, these authors[3] did not include the $v = 0$ level of the Rydberg ($A^2\Pi$)3sσ $W^1\Pi$ state. Note in this respect that Casey[2] also carried out a deperturbation which did include W($v = 0$) in a procedure that included altogether four $^1\Pi$ states ($L^1\Pi(4p\pi)v = 0$; $G^1\Pi(3d\pi)v = 1$; $W^1\Pi v = 0$, and an undefined $^1\Pi$ valence state). In a recent paper (ref 1) we referred to the perturbing valence state as $E'^1\Pi$. This state is likely described by the configuration $4\sigma^2 5\sigma 1\pi^3 2\pi^2$, the same valence configuration which describes $k^3\Pi$, the companion triplet state of $E'^1\Pi$.

TABLE 3: Spectroscopic Constants of the Ground and First Excited Valence States of $^{12}C^{16}O^{+a}$

state	configuration	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ref
(CO$^+$)X$^2\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4$	0.0	1.115217	2214.127	15.094	exp[31]
		0.0	1.119	2214.6	14.75	30
		0.0	1.111	2173.8	14.71	this work
(CO$^+$)A$^2\Pi_i$	$4\sigma^2 5\sigma^2 1\pi^3$	20732.037	1.24377	1561.806	13.4785	exp[31]
		20594.0	1.246	1570.0	12.86	30
		19928.5	1.2496	1574.5	19.2	this work

[a] Column 2 gives the dominant configuration.

A further deperturbation was also attempted by Eidelsberg et al.[3] including 4p($v = 2$), 5p($v = 0$) and two $^1\Pi$ valence states, one of which is probably a level of E$'^1\Pi$, whereas the other involves a level with a very small rotational constant ($B_v = 0.5$ cm^{-1}). The W$^1\Pi$ state was likewise overlooked in this latter deperturbation.

Unfortunately, as pointed out earlier,[1] the aforementioned local deperturbation procedures did not succeed in finding a global solution to the problem. Hence, it would be desirable to carry out a deperturbation employing the whole diabatic potential curves, followed by a coupled-equations treatment, analogous to the procedure performed earlier in N$_2$.[27,28]

States of the Ion CO$^+$

The most accurate value of the first ionization potential (IP) of CO, corresponding to CO$^+$ (X$^2\Sigma^+$, $v^+ = 0$, $N^+ = 0$), was obtained by laser-induced fluorescence[29] as 14.013 63 ± 0.000 04 eV. This value corresponds to T_e = 113 028.33 cm^{-1}. The best calculated value is that of Okada and Iwata of 112 830 cm^{-1};[30] our computed IP value is 112 723.2 cm^{-1}. The spectroscopic constants of the X$^2\Sigma^+$ and A$^2\Pi$ states of CO$^+$ are given in Table 3.

Technical Details of the Calculations

Our ab initio electronic structure calculations of CO are of the self-consistent field configuration interaction (SCF-CI) type and were carried out by employing the MRD-CI package,[10,32,33] which we have been using for several years (see, for instance, refs 34−36 and references therein). The atomic orbital (AO) basis set employed for the calculations is the aug-cc-pVQZ Gaussian basis set of Dunning[37] for both carbon and oxygen, but without the two g ($l = 4$) functions. This basic basis set was augmented with twelve diffuse functions, six per atom, corresponding to the 3s, 3p, 3d, 4s, 4p and 4d Rydberg atomic orbitals of both C and O.[38] The exponents for the C atom are those of Dunning and Hay,[38] namely, 0.023 (3s), 0.0055 (4s), 0.021 (3p), 0.0049 (4p), 0.015 (3d), and 0.0032 (4d). For the O atom the exponents of the diffuse functions 3p, 4s, and 4p were optimized, taking as starting point the exponents recommended in ref 38. The exponents we finally choose for oxygen are 0.032 (3s), 0.0022 (4s) rather than 0.0066, 0.031 (3p) instead of 0.028, 0.011 (4p) rather than 0.0054, 0.015 (3d) and 0.0032 (4d). The number of orbitals in carbon and oxygen is the same, 8s7p6d3f, which gives a total of 95 functions per atom. In the molecular framework these functions corrrespond, in C_{2v} symmetry, to 8 (a1), 7 (1a1, 1b1, 1b2), 6 (3a1, 1b1, 1b2, 1a2) and 3 (3a1, 3b1, 3b2, 1a2). The total number of atomic functions in our basis set is thus 190. The 1σ and 2σ molecular orbitals of CO, corresponding to the 1s atomic orbitals of C and O were kept doubly occupied in all CI calculations, so the number of active electrons in the CI treatment is 10. All calculations were carried out in C_{2v} symmetry.

Different sets of SCF MOs were tested as basis sets for the CI procedure to select the molecular orbital best fit for the calculations of the $^1\Sigma^+$ and $^{1,3}\Pi$ states. The SCF MOs of the following molecular states of CO, CO$^+$, and CO$^-$ were surveyed: CO (X$^1\Sigma^+$, 1 $^5\Sigma^-$), CO$^+$ (X$^2\Sigma^+$, A$^2\Pi$, 1 ^{4}A$_1$), and CO$^-$ (X$^2\Sigma^+$, 1 ^{4}A$_2$). Non-negligible differences were found among the various test cases. We plan to report the technical details and results of the various sets of calculations elsewhere. The SCF MOs that turned out to be the best fit to describe the 85 000−110 000 cm^{-1} region are, not so surprisingly, those of the cation, namely, the SCF MOs of X$^2\Sigma^+$ and A$^2\Pi$. Quite understandably, the MOs of these two states yield a satisfactory representation of the Rydberg states converging to the first two ionization limits. Furthermore, the CO$^+$ (X$^2\Sigma^+$, A$^2\Pi$) MOs yielded a more compact description of the Rydberg states, thus facilitating the assignment of their character. Hence, the $^1\Sigma^+$ states were computed employing the CO$^+$ (X$^2\Sigma^+$) MOs and the $^1\Pi$ and $^3\Pi$ states employing the CO$^+$ (A$^2\Pi$) MOs. The CO$^+$ (X$^2\Sigma^+$) state is described at the SCF level of approximation by $(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_1)^2(1b_2)^2(5a_1)^1$ in C_{2v} symmetry and by $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^1$ in $C_{\infty v}$ symmetry, and CO$^+$ (A$^2\Pi$) by $\cdots(4a_1)^2(5a_1)^2(1b_1)(1b_2)^2$ in C_{2v} symmetry and by $\cdots(4\sigma)^2(5\sigma)^2(1\pi)^3$ in $C_{\infty v}$. However, this choice is not without difficulties and implies compromises. The valence states, for instance, are less well described. Also, it is questionable whether the Rydberg-valence interaction is properly accounted for.

The CI treatment was carried out by employing a reference space of 212 ($^1\Sigma^+$ and $^1\Delta$), 314 ($^1\Pi$), and 305 ($^3\Pi$) configurations (depending on spatial symmetry and spin multiplicity), from which all single and double excitations were generated. The contribution of selected triple and quadruple excitations was accounted for by means of the Davidson correction.[39,40] An energy threshold of $T = 0.5$ μH was chosen to select the configurations to be included in the reference space. To ensure consistency at all internuclear distances we used, in most cases, a common reference space in the whole interval, 1.5−7.0 au for the $^1\Sigma^+$ and $^1\Delta$ states, and 1.5−5.75 au for the $^1\Pi$ and $^3\Pi$ states; the common space resulted from a merge of all configurations which in the respective interval contributed with $c_i^2 > 0.0020$. The configuration interaction treatment was carried out in two separate CI subspaces corresponding to the A$_1$ and B$_1$ irreducible representations. The A$_1$ irreducible representation yields Σ^+ states and the A$_1$ component of the doubly degenerated Δ states, while B$_1$ gives the Π states.

The number of generated spin-adapted functions (SAFs) is 35 × 10^6 ($^1\Sigma^+$ and $^1\Delta$ states), 58 × 10^6 ($^1\Pi$ states), and 106 × 10^6 ($^3\Pi$ states). The dimension of the matrices which were diagonalized directly is typically 452 × 10^3 ($^1\Sigma^+$ and $^1\Delta$ states), 460 × 10^3 ($^1\Pi$ states), and 365 × 10^3 ($^3\Pi$ states), all this depending on internuclear distance, spatial symmetry, and spin multiplicity. The sum of the squares of the coefficients of the reference configurations (Σc_i^2) in the CI treatment was typically 0.91−0.94. The energy obtained in a SCF calculation of the

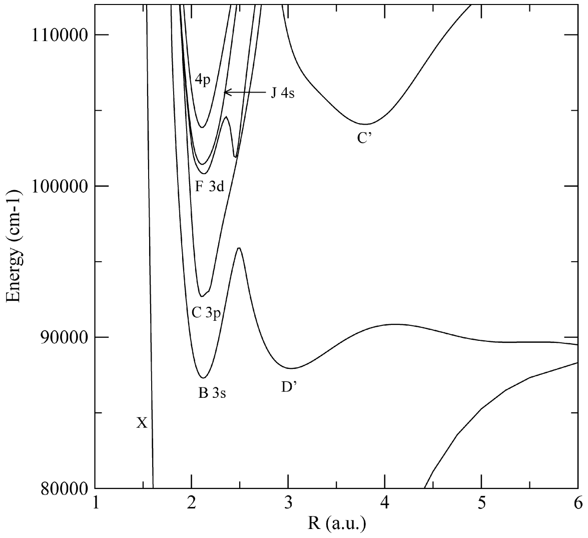

Figure 1. Potential energy curves of the $^1\Sigma^+$ states of CO.

$X^1\Sigma^+$ state at its experimental equilibrium distance of 1.128 32 Å (2.132 216 au)[13] and with its own SCF MOs is $E_{SCF} = -112.296\,136\,88$ hartree. Our estimated full-CI energy (E_{FCI}) of the CO($X^1\Sigma^+$) ground state obtained at the aforementioned equilibrium distance is $E_{FCI} = -113.176\,156\,58$ hartree, substantially lower (0.208 166 hartree or 5.66 eV) than the energy obtained by Cooper and Kirby[9] of −112.967 99 hartree, and also well below (0.068 714 hartree or 1.87 eV) the energy obtained by Chantranupong et al.[11] of −113.107 442 hartree.

The calculation of the spectroscopic constants of each state proceeds as follows: first we interpolate among the calculated energy points employing the Lagrange method. Then, we solve by numerical integration the nuclear Schrödinger equation for the first three vibrational levels of each state. Assuming that the Morse potential is a good approximation at the bottom of the curve(s), we obtain the constants ω_e and $\omega_e x_e$. For cases in which the shape of the potential energy curve deviates ostensibly from the Morse potential we report only the ΔG_0 value.

Singlet Σ^+ States

The $B^1\Sigma^+$ (3sσ) Rydberg State and the $D'^1\Sigma^+$ Valence State. Figure 1 depicts the computed potential energy curves of the $^1\Sigma^+$ states. The $B^1\Sigma^+$ adiabatic potential undergoes an avoided crossing with the $D'^1\Sigma^+$ potential. The B3sσ state is described by the configuration $4\sigma^2 5\sigma 1\pi^4 3s\sigma$ and the D′ state by $4\sigma^2 5\sigma^2 1\pi^3 2\pi$. The electrostatic coupling term between the B and D′ diabatic potentials is assumed to be one-half of the minimum energy gap between the two adiabatic curves.[41] The computed crossing point of the two diabatic potentials is at ∼1.32 Å, to be compared with the value of 1.307 Å resulting from the empirical curves of Tchang-Brillet et al.,[42] and with the value of 1.286 Å of ref 19. Our computed D′ adiabatic potential can hold four bound vibrational levels, in agreement with the number of observed levels.[43] Our computed coupling term of 3481 cm^{-1} is somewhat larger than the value of 2900 cm^{-1} of Tchang-Brillet et al.[42] The spectroscopic constants of the adiabatic potentials of B and D′ are reported in Table 4.

The $C^1\Sigma^+$ (3pσ) Rydberg State. The $C^1\Sigma^+$ Rydberg state is dominated by the $4\sigma^2 5\sigma 1\pi^4 3p\sigma$ configuration. The spectroscopic constants of the C state are given in Table 4. Our values are comparable to previous results.[11] The relative energy position of the minima of the C and D′ adiabatic curves is too large with respect to experiment. The calculated energy difference is 4748 cm^{-1} whereas the experimental value is 2476 cm^{-1} (see Table 1). Note, however, that Cooper and Langhoff[7] obtained a C−D′ energy difference of only 1592 cm^{-1}.

The $C'^1\Sigma^+$ Valence State. Our computed T_e for the C′ state, i.e., 104 127 cm^{-1} is substantially larger than the assumed experimental value,[3] 102 207 cm^{-1}; yet our R_e value is in closer agreement with the early results of Cooper and Kirby.[9] It is important to point out that the experimental data reported in Table 4 for the C′ state result from an extrapolation[3] and consequently are uncertain.

Singlet Π States. The results for the $^1\Pi$ states obtained with the CO$^+$ ($A^2\Pi$) MOs appear to be the easiest ones to be interpreted (see Figure 2 and Table 5). The left, lower minimum of the second calculated adiabatic $^1\Pi$ potential corresponds to the ($X^2\Sigma^+$)3pπ $E^1\Pi$ Rydberg state. The right, higher lying minimum of the same adiabatic potential can be viewed as another state, the E′ $^1\Pi$ valence state. E′ is described at its minimum (at ∼2.4 au) by a mixture of the two dominant configurations, $4\sigma 5\sigma^2 1\pi^4 2\pi$ and $4\sigma^2 5\sigma 1\pi^3 2\pi^2$, both of them of valence character; these two configurations correspond precisely to those describing the $b^1\Pi_u$ valence state of the isoelectronic N_2 molecule.[1]

At higher energies appears the $4\sigma^2 5\sigma^2 1\pi^3 3s\sigma$ configuration, which corresponds to the ($A^2\Pi$)3sσ Rydberg state. This configuration is precisely the one that describes the $W^1\Pi$ state. Yet, the computed potential curve of the $W^1\Pi$ state turns out to be strongly mixed with the 4dπ Rydberg and with the E′ valence states. The minimum of the $W^1\Pi$ state is obtained from a simulated diabatic curve plotted in dotted lines in Figure 2 (see also Table 5). Actually, the observed $W^1\Pi$ state is indeed rather perturbed, presumably by an interaction with an unidentified state.[3]

The key issue is to assign the observed $^1\Pi$ levels to vibrational levels of the calculated adiabatic E−E′ $^1\Pi$ state. The Π band observed at 98 921 cm^{-1} has been attributed to two different states. Eidelsberg and Rostas[25] assigned it to a level of the $^3\Pi$ state associated with the $W^1\Pi$ Rydberg species, whereas Eidelsberg et al.[3] have later assigned this feature to the $v = 3$ level of the $E^1\Pi$ Rydberg state which appears strongly perturbed by the mixing with other state(s).

By means of a numerical integration of the nuclear Schrödinger equation of the E−E′ adiabatic curve, we obtained vibrational levels with atypical ΔG_v values that decrease steeply with increasing vibrational quantum number (see Figure 3). A similar decrease in the first experimental vibrational intervals of the $E^1\Pi$ state has been noted by Eidelsberg et al.[3] who, following Cooper and Kirby,[22] have attributed this behavior to a mixing with a valence state described by the $1\pi^3 5\sigma 2\pi^2$ configuration. The uppermost calculated vibrational levels ($v \geq 5$) of the E−E′ adiabatic potential probably correspond to levels observed by Eidelsberg and Rostas[25] and Casey[2] at 100 651, 102 311 (the observed W′ $^1\Pi$ state of Drabbels et al.[26]), and 104 120 cm^{-1}. Note that the calculated adiabatic levels are only an approximation to the actual observed levels since our vibrational calculations ignore the nonadiabatic coupling.

Triplet Π States. The potential energy curves of the $^3\Pi$ states of CO are given in Figure 4. Three triplet states are expected in the energy region near 90 000 cm^{-1}, each of them corresponding to a different $^1\Pi$ state. The first triplet is the $c^3\Pi$ state associated with the ($X^2\Sigma^+$)3pπ $E^1\Pi$ state. The second one is the $^3\Pi$ state associated with the ($A^2\Pi$)3sσ $W^1\Pi$ state. In N_2 the energy difference between the corresponding singlet−triplet pair of Rydberg states, namely, the ($A^2\Pi_u$)3sσ $o^1\Pi_u$ singlet and

TABLE 4: Spectroscopic Constants of the $^1\Sigma^+$ States of $^{12}C^{16}O^a$

state	configuration	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ref
$B^1\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4 3s\sigma$	86926.9	1.1197	2161.7	39.8	exp[25]
		86382.6	1.105	2183.9	31.2	11
		87292.8	1.124	2093.0	15.7	this work
$D'^1\Sigma^+$	$4\sigma^2 5\sigma^2 1\pi^3 2\pi$	89438.4	1.583	651.4	20.4	exp[43]
		92673.7	1.519	974.4	7.3	7
		87912.0	1.614	681.7	13.4	this work
$C^1\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4 3p\sigma$	91914.0	[1.1248]	2189.0	17.33	exp[25]
		91786.5	1.120	2190.0	16.5	11
		92659.8	1.1215	2183.12	16.18	this work
$C'^1\Sigma^+$	$4\sigma^2 5\sigma^2 1\pi^2 2\pi^2$	(102207.0)	(1.7)	(718.0)	(−7.0)	exp[3]
		107595.0	1.91	(600)		9
		104127.3	1.935	709.3	46.7	this work
$F^1\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4 3d\sigma$	[99741.7]	[1.166]	[2025.8]		exp[25]
		100784.4	1.122	[2151.3]		this work
$J^1\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4 4s\sigma$	[101461.0]		[2230.0]		exp[25]
		101453.8	1.114	[2033.5]		this work
$^1\Sigma^+$	$4\sigma^2 5\sigma 1\pi^4 4p\sigma$	104015.0	1.113	[2231.1]		this work

[a] Column 2 gives the dominant configuration. Values in parentheses are uncertain. For the more perturbed states, T_0, R_0, and ΔG_0 values are given [in square brackets], rather than the equilibrium data T_e, R_e, ω_e, and $\omega_e x_e$.

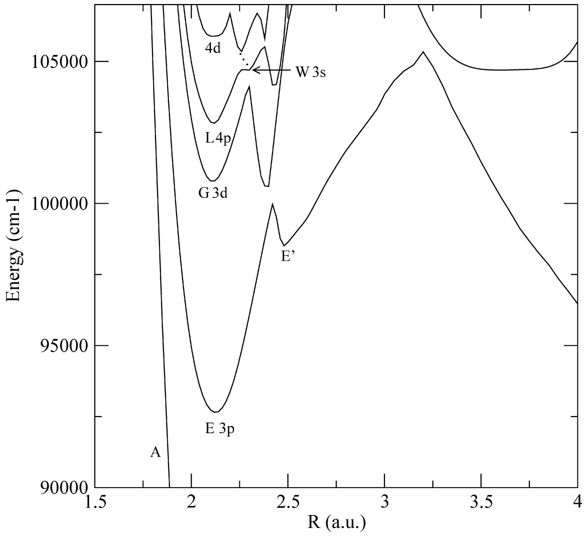

Figure 2. Potential energy curves of the $^1\Pi$ states of CO. The diabatic curve of the $W^1\Pi$ state is simulated by dots.

the companion triplet $F^3\Pi_u$ is 955.4 cm^{-1}. The $F^3\Pi_u - X^1\Sigma_g^+$ forbidden transition was observed optically for the first time in 2005.[46] Experiments locate the $v = 0$ level of $W^1\Pi$ at 102 806.4 cm^{-1}. Hence, by analogy with the singlet−triplet splitting in N_2, the triplet state of CO associated with the $W^1\Pi$ state is expected at about 101 850 cm^{-1}. This triplet state does not seem to have been recognized in the absorption spectrum in the neighborhood of this latter energy value. However, a low-energy electron spectroscopy study performed by Mazeau et al.[47] shows a peak at 12.53 ± 0.01 eV (101 062 ± 80 cm^{-1}), which could well belong to a $^3\Pi$ state. The calculations indicate that the $(A^2\Pi)3s\sigma$ $^3\Pi$ state is strongly mixed with the 4p and 4d Rydberg states. The minimum of this state is located at 101 376 cm^{-1}, in relatively good agreement with the expectation based on the N_2 analogy and the position of the experimental feature.[47]

The third expected triplet state is the valence state corresponding to the $E'^1\Pi$ state, namely, the observed $k^3\Pi$ state.[51] The adiabatic $^3\Pi$ curve located above the $a^3\Pi$ valence state presents two minima. By integration of the nuclear Schrödinger equation, using the Fox−Goldwin procedure, we have obtained successive vibrational levels of this adiabatic potential. We have attributed the third level of this double-well potential to $v = 0$ of the $c^3\Pi$ state and the sixth level to $v = 1$ of the same c state. The $v = 0$ and $v = 1$ vibrational levels of the $c^3\Pi$ state show strong homogeneous perturbations presumably caused by the $k^3\Pi$ state. These perturbations have been studied carefully by Baker and Launay[48] who were able to deduce an electronic perturbation parameter $H_e = 323 \pm 40$ cm^{-1}. The smallest energy difference between the second and third $^3\Pi$ adiabatic potentials is then expected to be roughly equal to $2H_e$.[41] Our calculated value is $2H_e = 852$ cm^{-1}, i.e., $H_e = 426$ cm^{-1}, in good agreement with the value of 323 cm^{-1} estimated by Baker and Launay.[48]

Directly above the k state appears another valence state, at about 99 611 cm^{-1}, and with an internuclear equilibrium distance of 1.40 Å (2.7 au). This state is described by a mixture of two dominant configurations, $4\sigma 5\sigma^2 1\pi^4 2\pi$ and $4\sigma^2 5\sigma 1\pi^3 2\pi^2$. This finding is not surprising since the configuration describing the k state, $4\sigma^2 5\sigma 1\pi^3 2\pi^2$, gives rise to four $^3\Pi$ states. In N_2, ab initio calculations have accounted for three $^3\Pi_u$ valence states. Comparison between the Figure 1 of Ndome et al.[49] and our Figure 4 shows that the C and C′ states of N_2 correspond to the c and k states of CO, respectively; and the N_2 III $^3\Pi_u$ state corresponds to the novel $^3\Pi$ state of CO which is, at the equilibrium distance of 2.7 au, the fourth calculated $^3\Pi$ state. The parallelism between the valence states of N_2 and CO is obvious. Table 6 compares our results for the $^3\Pi$ states with experimental data.

An accidental predissociation observed in the $E^1\Pi(3p\pi)$ state has already been discussed before,[1] and an explanation of this process has been proposed. An electronic interaction parameter of 200 cm^{-1} between the $k^3\Pi$ state and the repulsive $^3\Pi$ state leading to the $C(^3P) + O(^3P)$ dissociation limit (i.e., the III $^3\Pi$ state predicted by O'Neil and Schaefer)[4] was estimated in ref 1. Figure 4 shows that at 1.83 Å (3.46 au), the potential curve of the k state is very close to a repulsive curve (in a diabatic picture). The computed energy difference between the curves is 418 cm^{-1} or $H_e = 209$ cm^{-1}, in excellent agreement with the estimated value of 200 cm^{-1}.[1]

Conclusion

The current ab initio calculations which focus on the VUV spectral region of CO lead to three major conclusions:

First, the calculated $^1\Sigma^+$ potential energy curves have reproduced reasonably well the $B(3s\sigma)$ and $C(3p\sigma)$ Rydberg

TABLE 5: Spectroscopic Constants of the $^1\Pi$ States of $^{12}C^{16}O^a$

state	configuration	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ref
$A^1\Pi$	$4\sigma^2 5\sigma 1\pi^4 2\pi$	65075.8	1.2353	1518.2	19.4	exp[13]
		65654.0	1.243	1496.0	18.1	11
		64755.7	1.237	1461.2	4.4	this work
$E^1\Pi$	$4\sigma^2 5\sigma 1\pi^4 3p\pi$	[92929.9]	[1.1221]	[2152.9]		exp[44]
		91544.6	1.123	2153.0	33.4	11
		92649.4	1.122	[2127.6]		this work
$E'^1\Pi$	$4\sigma^2 5\sigma 1\pi^3 2\pi^2$	98487.7	1.313	[750.]		this work
$G^1\Pi$	$4\sigma^2 5\sigma 1\pi^4 3d\pi$	[101032.3]	[1.119]	[2178.9]		exp[25]
		100724.6	1.120	[2509.5]		this work
$W^1\Pi$	$4\sigma^2 5\sigma^2 1\pi^3 3s\sigma$	102967.7	[1.2548]	1864.4	47.55	exp[25]
		102960.0	1.26	[1477.0]		22
		104600	1.217			this work
$L^1\Pi$	$4\sigma^2 5\sigma 1\pi^4 4p\pi$	[103271.8]	[1.1201]	[2169.6]	(15.0)	exp[25,45]
		101239.7		2168.0	160.0	11
		102772.1	1.115	[1931.4]		this work
	$4\sigma^2 5\sigma 1\pi^4 4d\pi$	105800	1.118			this work

[a] Column 2 gives the dominant configuration. For the more perturbed states, T_0, R_0, and ΔG_0 are given [in square brackets], rather than T_e, R_e, ω_e, and $\omega_e x_e$.

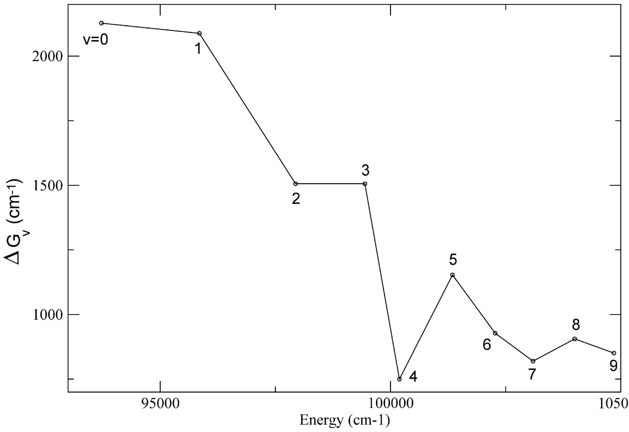

Figure 3. ΔG_v values of the vibrational levels of the E−E′ adiabatic curve of the second $^1\Pi$ state of $^{12}C^{16}O$.

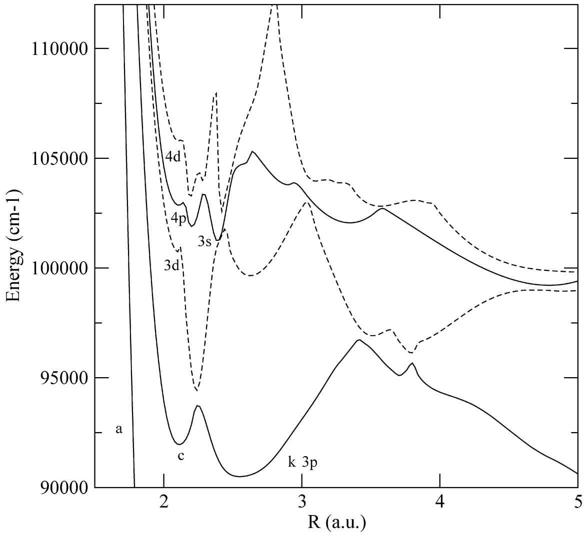

Figure 4. Potential energy curves of the $^3\Pi$ states of CO. The potential curves of the dπ Rydberg states are plotted in dashed lines for clarity.

states as well as the D′ and C′ valence states. The computed D′ state agrees relatively well with experiment while the C′ state is calculated to lie some 2000 cm^{-1} above the energy position inferred by experimentalists from an extrapolation procedure.[3]

TABLE 6: Spectroscopic Constants of the $^3\Pi$ States of $^{12}C^{16}O^a$

state	configuration	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ref
$a^3\Pi$	$4\sigma^2 5\sigma 1\pi^4 2\pi$	48686.7	1.2057	1738.26	14.25	exp[13,50]
		48877.5	1.207	1786.7		7
		48419.8	1.209	1757.1	25.4	this work
$k^3\Pi$	$4\sigma^2 5\sigma 1\pi^3 2\pi^2$	91012.2	1.379	805.1	−2.85	exp[51]
		96500.0	1.377			5, 52
		90491.4	1.333	[882.7]		this work
$c^3\Pi$	$4\sigma^2 5\sigma 1\pi^4 3p\pi$	[92076.9]	[1.1203]	[2190.]		exp[53]
		91948.5	1.116	[1948.9]		this work
$4^3\Pi$	$4\sigma^2 5\sigma 1\pi^3 2\pi^2$	99611	1.40	[1323.6]		this work
$5^3\Pi$	$4\sigma^2 5\sigma^2 1\pi^3 3s\sigma$	101376	1.27			this work

[a] Column 2 gives the dominant configuration. For the more perturbed states, T_0, R_0, and ΔG_0 are given [in square brackets], rather than T_e, R_e, ω_e, and $\omega_e x_e$.

Second, the second $^1\Pi$ potential displays a curve with two minima corresponding to the adiabatic curve resulting from the mixing of the $E^1\Pi$(3pπ) Rydberg state and the $E'^1\Pi$ valence state. The computed energy intervals between successive vibrational levels of the E−E′ adiabatic curve can explain the observed anomaly in the ΔG_v curve of the $E^1\Pi$ state, as well as the observation of several valence $^1\Pi$ levels perturbing the Rydberg p complexes.[2,3] It is clear that if pure valence and pure Rydberg diabatic potential curves are obtained, both with their mutual electrostatic interactions, the solution of a system of coupled equations[41] could probably yield energy levels comparable to the observed ones. We plan to undertake this study in the near future.

Finally, the $^3\Pi$ state associated with the $W^1\Pi$ state, that is, the lowest Rydberg species with a $A^2\Pi$ core and a 3sσ electron, is predicted to lie at 101 376 cm^{-1}.

The current calculations constitute a first step to study the wide variety of predissociation processes observed in CO.

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