J. Phys. B: At. Mol. Opt. Phys. **29** (1996) 6185–6201. Printed in the UK

R-matrix calculation of Rydberg states of CO

Jonathan Tennyson†

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Received 5 September 1996

Abstract. Valence and Rydberg bound states of CO are studied *ab initio* using the UK molecular *R*-matrix code and electron–CO^+ scattering calculations. Results are presented for singlet and triplet Σ^+ and Π states of CO at $R = 2.132\ a_0$. Various models for both the CO^+ target and the full calculation are tested and the stability of the final models is demonstrated. Final calculations employ complete active space (CAS) target states, with and without further excitation, and up to 13 target states in the close-coupling expansion. The best model underestimates the ionization potential of CO by 0.1 eV and finds quantum defects systematically slightly higher than those observed, by up to 0.07. The prospects for further improvement of these calculations are discussed.

1. Introduction

There have been a great many recent experimental studies of the Rydberg states of CO. Among these are spectroscopic observations of both singlet (Masaki *et al* 1987, Eidelsberg and Rostas 1990, Ebata *et al* 1992, Drabbels *et al* 1993, Eikema *et al* 1994, Baker *et al* 1995, Komatsu *et al* 1995, Ebata *et al* 1995) and triplet (Mellinger and Vidal 1995, Mellinger *et al* 1996) Rydberg states, photoionization studies (Hardis *et al* 1988, Dadouch *et al* 1991, Baltzer *et al* 1994), and studies using electron impact excitation (Hammond *et al* 1985, Cosby 1993, Zobel *et al* 1996) and Penning ionization (Lescop *et al* 1996). The high dissociation energy of CO means that its Rydberg states are particularly amenable to such studies which are particularly important, for instance in astrophysics (Eidelsberg and Rostas 1990).

Theoretically there has been much less work. The low-lying electronically excited states of CO, most of which have pronounced Rydberg character, were extensively studied using standard quantum chemical techniques by Kirby and co-workers (Cooper and Kirby 1987, 1988, Kirby and Cooper 1989, Rosenkrantz and Kirby 1989, Kirby *et al* 1992), and more recently by Chantranupong *et al* (1992). There appears to have been little attempt to study the higher-bound Rydberg states *ab initio* since Lefebvre-Brion *et al* (1964), although Singleton *et al* (1995) used CO to test a perturbation theory model for molecular Rydberg states, and Leyh and Raseev (1986, 1988) used a method with some similarities to the one used here to determine quantum defects for higher Rydberg series of CO. It should be noted that standard electronic structure methods, even those specially designed for Rydberg states (see Kaufmann 1991), are by their nature restricted to considering lower-lying Rydberg levels.

---

† On sabbatical at: Institute for Theoretical Atomic and Molecular Physics, Harvard–Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA and JILA, CB440, University of Colorado, Boulder, CO 80309-0440, USA

0953-4075/96/246185+17$19.50

For complex atoms and ions, scattering calculations have become a standard and reliable tool for obtaining bound state energies and wavefunctions. For example, this approach has been utilized with great success by the Opacity Project Team (1995). A number of similar R-matrix calculations have been tried for diatomic molecules (Tennyson 1988, Sarpal *et al* 1991, Branchett and Tennyson 1992, Rabadán and Tennyson 1996). These calculations gave excellent results for systems where one ‘scattering’ electron is bound to a ‘target’ ion with only one or two electrons (see Sarpal *et al* 1991). Studies involving more complex molecular ‘targets’ have proved more difficult. This is due to computational limitations which meant that, up until now, only very restricted treatments of the target wavefunction were possible.

Very recently a new algorithm has been developed (Tennyson 1996a) which greatly increases the size and sophistication of the target wavefunctions which can be used in such calculations. In this work the new algorithm is exploited to study the Rydberg states of the CO molecule by considering electron collisions with CO^+. An important aspect of this work is the development of robust, reliable and predictive models within the new framework; the first part of the paper is taken up with this problem. The latter part of the paper presents results for the important symmetries of CO and compares them with previous studies, both experimental and theoretical.

2. Calculations

2.1. General considerations

The R-matrix method divides configuration space into two regions. The inner region is defined by a sphere centred at the molecular centre-of-mass which is designed to enclose the entire N-electron target wavefunction. In these calculations a sphere of radius 10 a_0 was used. In the inner region, the wavefunction of the $(N+1)$-electron system is given by

$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \Phi_i(1, \ldots, N) F_{i,j}(N+1) + \sum_i b_{i,k} \chi_i(1, \ldots, N+1), \qquad (1)$$

where $\mathcal{A}$ is the antisymetrization operator, $F_{i,j}$ are continuum orbitals and χ_i are two-centre L^2 functions constructed from N-electron ‘target’ orbitals.

In (1), Φ_i is the wavefunction of the ith target state. Electron-correlation effects are included in these target wavefunctions via configuration interaction (CI) expansions:

$$\Phi_i = \sum_{m=1}^{M_i} c_{im} \eta_{im}(x_1 \ldots x_{N_i}) \qquad (2)$$

which have to be phase matched to the $(N+1)$-electron wavefunction (Tennyson 1996b). As target configurations, η_{im}, only appear in the $(N+1)$-electron wavefunction as particular linear combinations given by the target coefficient vector $\boldsymbol{c}_i$, it is necessary to contract matrix elements between individual configurations into linear combinations. It is the characteristic structure given to scattering calculations by this contraction step and relatively long continuum orbital expansion that the new SCATCI algorithm exploits (Tennyson 1996a).

Previous R-matrix calculations used rather limited target CI expansions and target wavefunctions were always obtained using a standard full matrix diagonalizer. This procedure is clearly inefficient for large CI expansions. To facilitate the present calculations a standard Davidson diagonalization procedure (Stathopoulos and Froese Fischer 1994) was implemented as part of our program suite (see Gillan *et al* 1995).

For many electron systems, for which full CI expansions and exact answers are impossible, a crucial factor in obtaining good results is the balance between the $(N+1)$-electron wavefunction of (1) and the N-electron wavefunction of (2). A well balanced calculation should be capable of systematic improvements which display convergence and should yield good results for properties, such as ionization potentials or quantum defects, which depend on differences between the two wavefunctions. Conversely treating the $(N+1)$-electron problem at a higher level than the N-electron problem may lead to lower energies, which are 'better' in a variational sense, but the loss of balance will result in the $(N+1)$-electron energies being too low compared to the N-electron ones. This phenomenon is well known in scattering calculations where it is generally described as 'over-correlation'.

Over-correlation can occur if the $(N+1)$-electron calculation includes configurations which improve the N-electron target wavefunctions. Such a calculation will lead to $(N+1)$-electron energies which are artificially lowered with respect to the N-electron target energies. As it is necessary for all target wavefunctions to be represented by a single orbital set, these improvements can take the form not only of correlation effects not covered by the target CI expansion, but also orbital relaxation effects. As will be shown below, this means that considerable care must be taken when constructing appropriate models.

2.2. *N-electron wavefunctions*

All calculations on both CO and the CO^+ 'target' were performed at the CO equilibrium bond length of $R = 2.132\ a_0$.

A variety of models for N-electron wavefunctions were tested in the course of this work; however, only results using four of these will be presented here. These wavefunctions all used the CO Slater-type orbitals of Kirby-Docken and Liu (1977) and the same natural orbitals (NOs). Two sets of NOs were initially obtained by performing full singles and doubles calculations from the lowest CO^+ SCF states with $^2\Sigma^+$ and $^2\Pi$ symmetry respectively.

Tests showed that, given the requirement to use a single orbital set, the energies were sensitive to the particular choice of NOs used. In particular, the CO^+ $X\,^2\Sigma^+ \rightarrow A\,^2\Pi$ excitation energy was found to vary between 3.0 and 6.0 eV in valence CAS calculations (see below) differing only in the NOs used. Finally a compromise set was chosen in which all σ and the 1π orbital were represented by the $^2\Sigma^+$ NOs and the remaining π and all δ orbital were represented by the $^2\Pi$ NOs. In all calculations the C and O 1s orbitals (1σ, 2σ MOs) were constrained to be fully occupied.

The simplest target model considered here is based on a valence CAS CI. The valence space was defined by the 3σ, 4σ, 5σ, 6σ, 1π, 2π orbitals and all configuration state functions (CSFs) arising from distributing the nine valence electrons among these orbitals were retained in our target expansion. This model gives 320 and 486 CSFs for $^2\Sigma^+$ and $^2\Pi$ symmetry respectively; this should be contrasted with the 616 and 588 CSFs obtained by Baltzer *et al* (1994) for the same model. This difference must be attributed to Baltzer *et al*'s use of C_{2v} symmetry whereas the Alchemy configuration generator (McLean 1971) employed here uses full $C_{\infty v}$ symmetry for linear heteronuclear molecules.

As will be demonstrated below, it is reasonably straightforward to construct a good scattering model on CAS-type wavefunctions. However, the valence CAS yields target excitation energies which are typically 0.4–1 eV too high for low-lying states (see table 1), and probably worse for higher states for which accurate comparative data are not available. It would, therefore, be highly desirable to include better target representations in the calculations.

Table 1. Vertical energy excitations (in eV) for the CO^+ target states used in the calculation at bond length 2.132 a_0. Also given are the absolute energy of the $X\,^2\Sigma^+$ground state in Hartree, the number of configurations, N, in each model and the leading multipole moments in au[a]. Literature values are given for comparison.

	Valence CAS	Extended CAS	CAS + singles	CAS + SD	CI[b]	CASSCF[c]	MCSCF-CI[d]	Experiment[e]
$N(^2\Sigma^+)$	320	2060	1310	1965	2253			
$X\,^2\Sigma^+$	−112.438 17	−112.463 50	−112.478 06	−112.492 52		−112.4453		
$B\,^2\Sigma^+$	6.81	6.84	6.05	6.44	6.29		5.3	5.8
$G\,^2\Sigma^+$	12.44	12.46	11.91	12.38	11.35		10.7	
$E\,^2\Sigma^+$	19.56	19.61	17.98	18.91	18.34			
$N(^2\Sigma^-)$	264			1845				
$^2\Sigma^-$	11.27			10.88				
$N(^2\Pi)$	486	3766	2280	3477	1269			
$A\,^2\Pi$	3.96	3.97	3.20	3.81	3.00	3.45	2.7	3.6
$^2\Pi$	11.13	11.13	10.45	10.60	12.44		8.0	10.4
$^2\Pi$	15.99	15.95	15.95	15.36	14.81		12.6	
$^2\Pi$	17.53	17.49	16.19	17.18	16.15			
$N(^2\Delta)$	276	3141	1624	2645				
$C\,^2\Delta$	11.34	11.35	10.65	10.90			8.5	~10.3
$^2\Delta$	14.31	14.27	13.68	14.32			10.6	
$^2\Delta$	21.24			21.19				
$N(^4\Sigma^+)$	164			1347				
$^4\Sigma^+$	8.38			8.37				
$N(^4\Sigma^-)$	196			1425				
$^4\Sigma^-$	10.53			10.25				
$N(^4\Pi)$	292			2515				
$^4\Pi$	12.41			12.00			11.7	
$N(^4\Delta)$	152			1889				
$^4\Delta$	9.70			9.51			7.2	
$\mu(X)$	0.99	0.99	0.97	1.03	1.01	1.01	1.0	
$\mu(A)$	−0.009	−0.008	0.06	0.01	0.10	0.10	0.05	
$\lvert\mu(A–X)\rvert$	0.25	0.25	0.28	0.23	0.38	0.38		
$\theta(X)$	−1.88	−1.89	−1.90	−1.90			−1.93	
$\theta(A)$	1.02	1.01	0.50	0.90			0.41	

[a] Positive dipoles point from C to O. Note that the sign convention for the multipole moments used here, and in other scattering calculations, is the opposite of that generally used in electronic structure calculations.

[b] POLCI calculations of Langhoff *et al* (1981).

[c] Interpolated from the CASSCF calculation of Martin and Fehér (1995).

[d] Lavendy *et al* (1993), excitation energies were estimated from figure 1.

[e] Vertical excitation energies estimated using the constants given by Huber and Herzberg (1979). Note that the ‘vertical excitation energies’ given in table 4 of Dadouch *et al* (1991), quoting the same source, are in fact adiabatic excitation energies, which are generally lower.

An obvious way of improving the valence CAS is simply to extend the active CAS space. A number of extensions were tried, but scattering calculations were performed only for the extended CAS in which the 1δ orbital was added to the active CAS space. This model was chosen in the hope that inclusion of a δ orbital in the CAS would improve both polarization in the Π symmetry calculations and the representation of the Δ symmetry target states. As shown in table 1, the number of CSFs used to represent each target state increases by almost an order of magnitude and the total energy of the states is lowered, almost uniformly, by 0.69 eV. The lack of improvement in the target excitation energies despite a large increase in the number of CSFs strongly suggests that this is not an efficient way forward.

The standard quantum chemical method of further correlating a valence CAS is to consider single and double excitations from that valence space into the remaining target orbital space. This can be done either using conventional multi-reference CI, or by using perturbation theory such as in the CASPT2 method (see Andersson *et al* 1990). For diatomics, such as CO^+, many millions of configurations are routinely considered in structure calculations. Here consideration is restricted to a model where the valence CAS was augmented by either single or single and double excitations into a limited space of target virtual orbitals.

Two such models were considered. Both models augmented the valence CAS with further excitations, all of which froze two electrons in the 3σ orbital. The CAS + singles model included excitations of the type $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7 \rightarrow (4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^6(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$. Both single and double excitations were included in the CAS + SD model, these consisted of CSFs $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7 \rightarrow (4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^6(7\sigma, 3\pi, 1\delta)^1$ and $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7 \rightarrow (4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^5(7\sigma, 3\pi, 1\delta)^2$.

The CAS + singles model not only gave a lower absolute energy than the other models, but significantly better excitation energies. This is undoubtedly due not only to increased correlation effects but to relaxation of the single orbital set constraint which is a result of including the single excitations. It should be noted that the CAS + singles models used larger space for the single excitations than the CAS + SD model. Of course use of the enlarged space for the CAS + SD model, would result in even lower absolute energies; however, for reasons discussed below, this was not computationally practical.

Table 1 gives details of target energies for all target states included in the various close-coupling calculations below. Comparison is made with the limited experimental data for this system and with *ab initio* electronic structure calculations.

There appear to be only two high-quality electronic structure calculations available for CO^+ (Lavendy *et al* 1993, Martin and Fehér 1995), of which only Lavendy *et al* consider several excited states. Lavendy *et al*'s MCSCF calculation is augmented by perturbation theory which appears to lead to an underestimate of all excitation energies by between 0.5 and 2.4 eV at $R = 2.132\ a_0$. Conversely our models overestimated the excitations energies between 0.4 and 1 eV for the pure CAS models, while the CAS + singles model gave energies all within 0.4 eV of experiment. The CAS + SD results fall in between the other models. It is likely that the excitation energies to the higher states are more seriously overestimated in all models.

Table 1 also makes some comparison of target moments with other available theoretical data. The agreement is reasonable.

2.3. $(N + 1)$-electron models

Most calculations used 14 CO^+ natural orbitals $(8\sigma, 4\pi, 2\delta)$, although the effect of removing or adding orbitals to this list is discussed below. These 'L^2' orbitals were augmented by continuum orbitals, $F_{i,j}$ in (1), expressed as a truncated partial wave expansion around the centre of mass. Partial waves with $l \leqslant 6$ and $m \leqslant 2$ were retained in this expansion.

The radial parts of the continuum functions were generated as numerical solutions of an isotropic Coulomb potential. Those solutions with an energy below 10 Ryd were retained. A Buttle (1967) correction was used to correct for the effect of this truncation or, alternatively, the fixed boundary condition used to generate the functions. It should be noted that while all other aspects of the calculation presented here are variational, the Buttle correction is perturbative and therefore can lead to non-variational behaviour. In practice such effects are small and none larger than 0.01 eV was observed in these calculations.

Clearly the continuum orbitals are not orthogonal to the CO^+ orbital set described above. To mitigate linear dependence effects two σ and one π continuum orbital were removed using Lagrange orthogonalization (Tennyson *et al* 1987). The resulting set of continuum orbitals had 62 σ, 52 π and 42 δ functions which were Schmidt orthogonalized to the target orbitals set.

The 'L^2' functions χ_i in (1) are constructed from the target orbitals and hold both the projectile and target electrons. These functions are of two types: those where the scattering electron enters the target CAS, which relaxes the enforced orthogonality between the target and continuum orbitals (orthogonality relaxing configurations), and those where the scattering electron occupies the extra target virtual orbitals which are introduced to allow for high ℓ effects near the nuclei and which compensate for the truncated partial wave expansion. In scattering calculations, these latter CSFs are usually denoted correlation configurations.

Both types of 'L^2' configurations also allow for relaxation (polarization) of the N-electron target wavefunction in the presence of the extra electron. One danger that has to be considered is that such configurations might help to correlate the target wavefunction as well as allowing it to respond to the presence of the extra electron. This is not possible for $(N+1)$-electron CAS CSFs of the type $(3\sigma, 4\sigma, 5\sigma, 1\pi)^{10}$ as the target electrons have already been fully correlated within this orbital space. However, the situation for the correlation configurations is not so simple and will be discussed further below. It is also harder to define orthogonality relaxing configurations for target wavefunctions not based on a CAS representation.

Single excitations from the target CAS give rise to orthogonality relaxing configurations of two types: $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$ and $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^6(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^2$. As these configurations involve all the L^2 orbitals used in the calculation, this means there are no correlation configurations left. However, using only these orthogonality relaxing configurations would neglect correlation configurations of the type $3\sigma^1(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^8(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$ and $3\sigma^0(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^9(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$ which were included in the pure CAS models. As the $7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta$ orbitals are no longer external to the target wavefunction, these configurations are not pure correlation configurations and cannot be contracted with the target wavefunction. Two models are presented for the CAS + singles calculation: model a which neglected 3σ correlation effects and model b which included them. A similar situation arises in the CAS + SD calculation. In this case model a contained orthogonality relaxing configurations of the same type as the CAS + singles model a. Model b included 3σ correlation effects and orthogonality relaxing configurations of the type $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^5(7\sigma, 3\pi, 1\delta)^3$.

The most extensive test calculations were performed using the valence CAS target wavefunctions for CO states with $^1\Sigma^+$ and $^1\Pi$ symmetry. Calculations were performed using a variety of target states in the close-coupling expansion, (1). In particular, 2-state calculations coupled target states $\mathrm{X}\,^2\Sigma^+$ and $\mathrm{A}\,^2\Pi$; 4-state calculations coupled target states $\mathrm{X}\,^2\Sigma^+$, $\mathrm{B}\,^2\Sigma^+$, $\mathrm{A}\,^2\Pi$ and $\mathrm{D}\,^2\Pi$; 6-state calculations involved the lowest three $^2\Sigma^+$ and $^2\Pi$ target states. In the 8-state model these were augmented by the lowest two states of $^2\Delta$ symmetry. An 11-state model used the lowest four $^2\Sigma^+$ and $^2\Pi$ target states and the lowest three $^2\Delta$ states. For $^1\Pi$ symmetry, a 12-state model was given by adding the lowest $^2\Sigma^-$ state to the 11-state model.

For triplet states of CO, it is also necessary to include quartet states of CO^+ in the close-coupling expansion. The $^3\Sigma^+$ and $^3\Pi$ calculations described below were based on the 8-state model used in the singlet calculations augmented by the lowest states of $^4\Sigma^+$, $^4\Pi$ and $^4\Delta$ symmetry, giving an 11-state model for $^3\Sigma^+$ calculations. For $^3\Pi$ states, the lowest $^2\Sigma^-$ and $^4\Sigma^-$ states of CO^+ were also added giving a 13-state model. Calculations analogous to the 11-state/12-state model used for the singlet symmetries were not attempted.

The effects of the different target wavefunctions and orthogonality relaxing models were tested for singlet symmetries using the 8-state model, as were the effects of the correlation orbitals on the calculation. Calculations were performed with no, two and four σ and π correlation orbitals. In these and all other calculations, the correlation orbitals were contracted in the same manner as the continuum orbitals (see section 2.1). However, in one calculation the effect of not contracting the correlation orbitals was also tested.

2.4. Bound states

Given the scattering formalism discussed above, it is necessary to have a method of finding bound state solutions in terms of wavefunction (1). These inner region solutions are used to construct an R-matrix on the boundary. In the outer region, in addition to the Coulomb potential, the potential was given by the diagonal and off-diagonal dipole and quadrupole moments of the CO^+ target states. The R-matrices were propagated (Morgan 1984) in this potential until the wavefunction could be matched with exponential decreasing functions obtained from a Gailitis expansion (Noble and Nesbet 1984). In this work R-matrices were propagated to 50 a_0.

Bound states were found using the searching algorithm of Sarpal *et al* (1991) with the improved nonlinear, quantum defect based grid of Rabadán and Tennyson (1996). This grid proved very efficient at isolating the cluster of states with small quantum defects at higher n. Indeed, contrary to previous calculations, no states appeared to be missed in any of our calculations and the searching algorithm was able to resolve four bound states in an energy range of less than 1 meV without any special choice of parameters.

For the larger close-coupling expansions, not all target states were explicitly included in the outer region. Tests showed that removing high-energy target states made a negligible difference to the bound-state energies obtained, while leading to considerable CPU time savings and improved stability in the propagation step of the calculation. Similarly, the $^2\Sigma^-$ and quartet states, which do not couple to the CO^+ $X\,^2\Sigma^+$ target state at long range, were omitted in the outer region.

3. Results

3.1. Stability of the model

Whilst comparing results of different calculations a number of properties were monitored. These included the absolute energy of the CO ground state, which is important for indicating how good the calculation is in a variational sense; the ionization potential (IP) of the CO ground state, which is sensitive to the relative treatment of the N and $(N+1)$-electron problems; the excitation energies of CO, particularly for valence states; and quantum defects, particularly for Rydberg states. For assignment purposes, the effective quantum number, v, is used instead of the quantum defect, α. These are related by

$$v = n - \alpha \tag{3}$$

where n, the principal quantum number, is an integer.

Table 2. Vertical energy excitations (in eV) and effective quantum numbers for excited states of CO for an 8-state calculation as a function of CO^+ wavefunction, see text for details. The absolute energy of the ground state is given in Hartree, as well as the ground-state ionization potential in eV.

	Valence CAS	Extended CAS	CAS + singles[a]	CAS + singles[b]	CAS + SD[a]	CAS + SD[b]
$^1\Sigma^+$						
	−112.938 78	−112.963 86	−112.971 94	−112.990 38	−112.993 49	−113.001 49
2pσ	13.62 0.999	13.61 1.000	13.44 1.006	13.94 0.988	13.63 0.999	13.85 0.991
2sσ	10.59 2.117	10.58 2.119	10.52 2.157	10.92 2.142	10.59 2.115	10.74 2.110
3pσ	11.15 2.344	11.14 2.345	10.99 2.355	11.33 2.284	11.15 2.340	11.36 2.336
3dσ	12.07 2.962	12.06 2.962	11.90 2.976	12.40 2.969	12.08 2.963	12.29 2.958
4sσ	12.25 3.148	12.24 3.149	12.09 3.178	12.58 3.163	12.26 3.146	12.47 3.140
4pσ	12.43 3.374	12.42 3.375	12.25 3.386	12.75 3.379	12.43 3.369	12.65 3.356
4dσ	12.75 3.957	12.75 3.958	12.58 3.974	13.07 3.964	12.76 3.959	12.98 3.952
4fσ	12.77 3.992	12.76 3.992	12.58 3.392	13.09 3.992	12.78 3.993	13.00 3.993
$^1\Pi$						
2pπ	9.31 1.777	9.31 1.779	8.99 1.750	9.02 1.663	9.17 1.746	9.19 1.709
3pπ	11.31 2.428	11.31 2.430	11.17 2.447	11.31 2.424	11.31 2.424	11.51 2.412
3dπ	12.18 3.070	12.17 3.071	12.00 3.075	12.17 3.067	12.19 3.069	12.40 3.063
4pπ	12.46 3.423	12.45 3.424	12.29 3.444	12.45 3.427	12.47 3.419	12.68 3.412
4fπ	12.77 3.993	12.76 3.993	12.59 3.993	12.76 3.993	12.78 3.994	13.00 3.993
4dπ	12.81 4.083	12.80 4.084	12.75 4.090	12.80 4.081	12.82 4.083	13.03 4.076

[a] Model a, see text for details.
[b] Model b, see text for details.

Before discussing results for different scattering models, it is worth considering the effect of different target representations on the calculation. Table 2 presents results for the four target models given in section 2.2.

A notable result of table 2 is the great similarity between the calculations performed with the valence and extended CAS target states. The extended CAS gives absolute energies which are 0.69 eV lower than the valence CAS, but none of the CO energy differences in the calculations change by more than 0.01 eV. This stability with respect to target state suggests that scattering calculations based on the CAS target states are indeed correctly constructed.

This stability is all the more remarkable when viewed in terms of the parameters of the calculation. Calculations that do not consider 'L^2' configurations which allow the 'scattering' electron to enter the target CAS give very poor results. The calculations using the extended CAS target states generate an order of magnitude more such CSFs, 2581 for the $^1\Pi$ symmetry calculation, than the valence CAS, which gives only 240 for a $^1\Pi$ calculation. As these extra CSFs inflate the size of the final Hamiltonian matrix, for which *all* eigenvectors are required, from 834 to 3175, calculations based on the extended CAS target states will not be considered further.

The final columns of table 2 show the results of calculations using the CAS + singles and CAS + SD models. In both models the absolute energies are significantly lower than the pure CAS models discussed above. However, as mentioned above, there is more difficulty in determining the correct 'L^2' CSFs to use with these targets. With the minimal orthogonalization relaxation effects given by model a in each case, neither of these models improve on relative energies given by the CAS target calculations. Indeed the CAS + singles model appears worse than, and the CAS + SD remarkably similar to, the CAS calculations.

With the inclusion of all possible orthogonalization relaxation CSFs, model b in each case, the situation changes somewhat. Superficially the CAS + singles calculations appear greatly improved. Indeed the IP is now within 0.1 eV of the experimental value and the $A\,^1\Pi$ $2p\pi$ excitation energy is significantly better. However the IP is actually too good. As will be seen below, the 8-state model used for these tests does not converge the IP to within 0.1 eV and there is little doubt that the absolute energy for the CAS + singles, model b ground state is too low.

This result is not unexpected. The problem is that of balance. The CAS + singles model improves the calculation in a variational sense but it is hard to construct a balanced model using this target wavefunction. In particular the target configurations of the type $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$ imply correlation configurations of the type $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^2$. These CSFs can be thought of as an admixture between CSFs arising from $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^7(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^1$ plus an electron, and $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^6(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^2$ plus an electron. While the former are those needed to relax orthogonality constraints in the calculation, the latter correspond to double excitations of the leading target (CO^+) configurations and can, therefore, be expected to lower significantly the energy of the CO^+ target states. It is just such behaviour that a well balanced calculation should avoid and calculations with the CAS + singles target wavefunctions were not pursued.

Conversely, the CAS + SD model b calculations presented in the final column of table 2 appear to improve on the simple CAS models without the problems associated with the CAS + singles calculations. In this case the potentially dangerous orthogonality relaxing CSFs are of the type $(4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi)^6(7\sigma, 8\sigma, 3\pi, 4\pi, 1\delta, 2\delta)^3$. These too have the ability to contribute towards the target correlation, although this contribution is via triple excitations out of the target CAS. Triple excitations, while not completely negligible, are known to be less significant than the double excitations which caused problems in the corresponding CAS + singles calculations. For this reason the CAS + SD, model b was adopted, along with the valence CAS model, to give final results.

Table 3 presents results as a function of close-coupling expansion. At first sight the convergence behaviour shown by this table is somewhat unusual as the excitation energies of the low-lying states, particularly the $A\,^1\Pi$ $2p\pi$ state, drop as the model is improved, while the excitation energies of the higher states rise in a rather uniform manner.

This differential convergence is intrinsic to the scattering method of finding bound states. It is a direct consequence of the fact that even a crude but correctly constructed scattering calculation will give reasonable predictions for the position of pure Rydberg states of the system relative to ionization, but poor results for the low-lying valence states.

Although widely ignored in *ab initio* calculations of Rydberg states, a crucial parameter in these studies is the IP of the system. For CO one can estimate the experimental vertical IP of CO at $R = 2.132\ a_0$ using constants from Huber and Herzberg (1979) as 14.03 eV. It can be seen that the valence CAS calculation approaches this value as the number of states considered is increased but that the best calculation, employing an 11-state model, still gives an IP 0.3 eV too small. The corresponding 11-state CAS + SD, model b calculation gives an IP of 13.90 eV, just 0.13 eV below experiment.

Among the *ab initio* calculations cited, only Langhoff *et al* (1981) quote an IP; they obtain a value of 13.44 eV with a calculation which could clearly be improved with today's technology. It is likely that an underestimate of 0.1 eV is competitive or better than the best of the various *ab initio* calculations on CO Rydberg states discussed below, although in the absence of data such an assertion must be considered speculative.

Table 3. Vertical energy excitations (in eV) and effective quantum numbers for excited states of CO as a function of number of states in the close-coupled expansion. The absolute energy of the ground state is given in Hartree, as well as the ground-state ionization potential in eV.

	2-state	4-state	6-state	8-state	11-state	12-state
$^1\Sigma^+$						
	−112.916 05	−112.927 45	−112.933 26	−112.938 78	−112.943 29	
2pσ	13.00 1.023	13.31 1.011	13.47 1.005	13.62 0.999	13.74 0.995	
2sσ	10.01 2.133	10.30 2.127	10.44 2.117	10.59 2.117	10.69 2.112	
3pσ	10.55 2.354	10.85 2.351	11.00 2.346	11.15 2.344	11.24 2.335	
3dσ	11.46 2.973	11.76 2.969	11.92 2.962	12.07 2.962	12.18 2.956	
4sσ	11.64 3.160	11.95 3.155	12.10 3.148	12.25 3.148	12.36 3.143	
4pσ	11.81 3.383	12.12 3.380	12.28 3.376	12.43 3.374	12.54 3.366	
4dσ	12.14 3.969	12.45 3.965	12.60 3.958	12.75 3.957	12.87 3.950	
4fσ	12.15 3.994	12.46 3.993	12.62 3.992	12.77 3.992	12.89 3.991	
5sσ	12.22 4.168	12.52 4.163	12.68 4.157	12.83 4.156	12.95 4.151	
$^1\Pi$						
2pπ	9.41 1.946	9.45 1.878	9.40 1.828	9.31 1.777	9.21 1.733	9.20 1.731
3pπ	10.87 2.528	11.08 2.473	11.20 2.449	11.31 2.428	11.40 2.412	11.40 2.411
3dπ	11.59 3.102	11.88 3.088	12.03 3.076	12.18 3.070	12.29 3.063	12.29 3.063
4pπ	11.89 3.498	12.17 3.454	12.32 3.473	12.46 3.423	12.57 3.412	12.57 3.412
4fπ	12.15 3.995	12.46 3.995	12.62 3.993	12.77 3.993	12.89 3.992	12.89 3.992
4dπ	12.20 4.114	12.50 4.101	12.66 4.089	12.81 4.083	12.93 4.076	12.93 4.076

The fact that the A $^1\Pi$ 2pπ state excitation energy decreases with increasing close-coupling expansion means that this valence state is even more poorly represented in the crude scattering calculation than the X $^1\Sigma^+$ ground state. Indeed it will be seen below that the present calculations perform particularly poorly for this state, with the best calculation still overestimating the X $^1\Sigma^+ \rightarrow$ A $^1\Pi$ excitation energy by 0.7 eV. The state A $^1\Pi$ 2pπ shows much greater sensitivity than the other states to the inclusion of states of $^2\Delta$ symmetry in the close-coupling expansion. As the representation of the C $^2\Delta$ state of CO$^+$ employed here is probably worse than that of the other low-lying CO$^+$ states, this is one aspect of the calculation which should be improved if a better representation of the A $^1\Pi$ 2pπ state is desired.

For higher states with purely Rydberg-like behaviour it is more useful to consider convergence of the calculation with respect to the ionization threshold as represented by the quantum defects, rather than excitation energies which essentially reflect the behaviour of the ground state IP. Table 3 shows that the $^1\Sigma^+$ quantum defects are not sensitive to the inclusion of $^2\Delta$ states while the $^1\Pi$ states are not sensitive to the addition of a $^2\Sigma^-$ state, observations which are consistent with the role of these states in providing polarization effects. Inclusion of $^2\Sigma^+$ and $^2\Pi$ states leads to a steady decrease which is clearly not completely stable even with the 11-state model.

It is computationally relatively cheap to include further excited states of the same symmetry in the calculation. However, this was not attempted because there are difficulties associated with this. The higher target states generated by the procedures outlined above become increasingly unphysical and, thus, any apparent convergence achieved may be simply an artefact of this. Furthermore, inclusion of all states in this expansion would necessarily lead to inclusion of all the associated correlation configurations which is equivalent to using all these configurations uncontracted. Tests discussed below show that use of all these configurations leads to an unbalanced calculation. Indications from recent electron–molecule scattering calculations are that such close-coupling expansions only converge slowly (Rescigno 1994). The generation of more complete expansions, along the lines that have recently been proved successful for atoms (Bray and Stelbovics 1995), will be the subject of future work.

More limited tests of convergence with respect to close-coupling expansion were also performed for the triplet states of CO. These showed somewhat different behaviour to that described for the singlet states. In particular, quite reasonable excitation energies for low-lying states were found with a 2-state (CO^+ states $X\,^2\Sigma^+$ and $A\,^2\Pi$) calculation. However, the triplet quantum defects were almost unchanged between this 2-state calculation and an 8-state (three $^2\Sigma^+$, three $^2\Pi$ and three $^2\Delta$ states) calculation. As the $X\,^1\Sigma^+$ ground state is lowered by 0.6 eV between the 2- and 8-state models, this leads to a corresponding increase in excitation energies. The 11-state model obtained by including the lowest CO quartet states of each symmetry ($^4\Sigma^+$, $^4\Pi$ and $^4\Delta$) leads to a significant reduction in both the excitation energies and the quantum defects. Addition of the lowest CO^+ $^2\Sigma^-$ and $^4\Sigma^-$ state to the $^3\Pi$ calculation to give a 13-state model also led to significant further reductions, 0.12 eV in the $X\,^1\Sigma^+ \rightarrow a\,^3\Pi$ excitation energy for example. This is in contrast to the $^1\Pi$ symmetry calculation which was insensitive to the inclusion of the lowest $^2\Sigma^-$ state.

As a final test of the model used here, the role of the so-called correlation configurations was explored. Similar tests were performed by Gillan *et al* (1996) for electron–N_2 scattering calculations; the tests performed here are not only more extensive, but are performed using more complex target wavefunctions. Furthermore, tests performed on purely bound states have a number of advantages when determining what constitutes a better calculation.

The calculations presented in table 4 show a remarkable stability with respect to the number of contracted correlation orbitals employed. The difference between using no σ or π correlation orbitals or using the $7\sigma, 8\sigma, 9\sigma, 10\sigma, 3\pi, 4\pi, 5\pi, 6\pi$ orbitals is small: 0.03 eV in the IP, and a maximum of 0.1 eV in the excitation energies. This stability mirrors the results of Gillan *et al* (1996), but is at odds with a number of earlier, cruder calculations which have found much sensitivity to the number of correlation orbitals used, see Salvini *et al* (1984) for example.

Significantly, calculations prior to those by Gillan *et al* (1996) have not usually contracted the correlation orbitals using the target wavefunctions. The final column of table 4 presents a $^1\Sigma^+$ calculation for which the correlation orbitals were not contracted. This calculation bears all the hallmarks of being unbalanced, in particular the IP is now significantly overestimated. The problem here is that, even within a CAS target model, these correlation configurations have some N-electron character arising from single excitations of the target wavefunction. It is this improvement of the target wavefunction which leads to the overestimate of the IP. Conversely, contracting minimizes, but does not completely eliminate, the contribution of the correlation orbitals to the target wavefunctions.

3.2. *Comparison with previous results: singlet states*

Table 5 summarizes various theoretical calculations on the excitation energies of the low-lying states of CO. For the higher of these states there does not appear to be complete consensus on the designation (as opposed to the symmetry) of the states. Where possible the designations given in Huber and Herzberg (1979) have been followed for tables 5–7. The latter two tables give comparisons with higher CO Rydberg states characterized by quantum defect analysis.

The best *ab initio* calculation available for CO excitations appears to be that of Chantranupong *et al* (1992), column e, who only considered singlet states. The exception

Table 4. Vertical energy excitations (in eV) and effective quantum numbers for excited states of CO for an 8-state calculation as a function of treatment of correlation configurations. The absolute energy of the ground state is given in Hartree, as well as the ground-state ionization potential in eV.

	No correlations[a]	Two correlations	Four correlations	Two correlations[b]
$^1\Sigma^+$				
	−112.938 07	−112.938 78	−112.938 94	−112.938 78
2pσ	13.60 1.000	13.62 0.999	13.63 0.999	14.91 0.955
2sσ	10.55 2.112	10.59 2.117	10.59 2.117	11.81 2.095
3pσ	11.12 2.343	11.15 2.344	11.15 2.345	12.41 2.333
3dσ	12.05 2.962	12.07 2.962	12.07 2.961	13.34 2.948
4sσ	12.23 3.144	12.25 3.148	12.25 3.146	13.51 3.122
4pσ	12.41 3.372	12.43 3.374	12.43 3.374	13.70 3.363
4dσ	12.73 3.958	12.75 3.957	12.76 3.957	14.03 3.930
4fσ	12.75 3.992	12.77 3.992	12.77 3.992	14.05 3.992
5sσ	12.81 4.153	12.83 4.156	12.84 4.156	14.11 4.126
$^1\Pi$				
2pπ	9.39 1.797	9.31 1.777	9.29 1.772	
3pπ	11.32 2.443	11.31 2.428	11.31 2.426	
3dπ	12.16 3.074	12.18 3.070	12.18 3.069	
4pπ	12.45 3.430	12.46 3.423	12.46 3.422	

[a] Number of σ and π correlation orbitals included in the calculation.

[b] Correlation configurations not contracted with the N-electron wavefunction.

of the A $^1\Pi$ state, discussed above, the 11-state valence CAS calculation gives excitation energies which lie within 0.2 eV of those obtained by Chantranupong *et al* (1992). The 11-state CAS + SD results are all within 0.1 eV of those of Chantranupong *et al* and are very close to the experimental estimates. It is interesting to note, however, that although Chantranupong *et al* present results for the lowest three $^1\Pi$ states obtained in their calculation, these do not correspond to the lowest three $^1\Pi$ states of CO. The state omitted is the 3dπ G $^1\Pi$ state which is reproduced here and is well known from spectroscopic studies (Ogawa and Ogawa 1974, Eidelsberg and Rostas 1990). This omission is a reflection of the difficulty of representing Rydberg states in conventional *ab initio* electronic structure calculations; essentially each Rydberg state requires its own specially designed basis functions (Kaufmann 1991).

Table 6 compares the present quantum defects with previous ones for singlet Rydberg states of CO. Only states which have been observed experimentally have been included in this table. Only states with $l \leqslant 3$ have been observed, whereas our R-matrix calculation gives states with l up to 6. All the experimental results quoted are for the vibrational ground state of the particular Rydberg state.

The $l \leqslant 2$ Rydberg series of CO have been very well studied experimentally and there is fair, if not total, agreement between various measurements over the values of the quantum defects. In contrast to NO (Rabadán and Tennyson 1996), there does not appear to be any outstanding assignment problems. Our quantum defects are uniformly higher than the observed values by up to 0.08 and 0.07 for the valence CAS and CAS + SD calculations respectively. In both cases the trends are well reproduced. Thus, for example, our quantum defects increase with n down the npσ $^1\Sigma^+$ series and decrease down all others, in agreement with observation. However, in both calculations the quantum defects for the npπ $^1\Pi$ series are nearly constant with n, while experimentally a general decrease with n is observed. The

Table 5. Vertical energy excitations (in eV) for excited states of CO at $R = 2.132\ a_0$. Also given is the absolute energy of the ground state in Hartree.

	Experiment	Theory				
	a	b	c	e	f, g	h, g
X $^1\Sigma^+$			−112.967 99	−113.107 94	−112.943 19	−113.003 39
B $^1\Sigma^+$	10.78	10.96	10.52	10.75	10.69	10.84
C $^1\Sigma^+$	11.40	11.54	11.03	11.40	11.24	11.39
F $^1\Sigma^+$		12.82			12.18	12.34
J $^1\Sigma^+$		13.52			12.54	12.52
A $^1\Pi$	8.51	8.53	8.83	8.68	9.20	9.24
E $^1\Pi$	11.53	11.65	11.45	11.37	11.40	11.55
G $^1\Pi$		13.47			12.29	12.45
L $^1\Pi$				12.65	12.57	12.73
G′ $^1\Pi$		13.68			12.89	13.05
a′ $^3\Sigma^+$	8.51	8.02			9.60	9.34
b $^3\Sigma^+$	10.4	10.58			10.21	10.46
j $^3\Sigma^+$	11.3	11.43			11.04	11.31
g $^3\Sigma^+$		13.13			12.01	12.29
h $^3\Sigma^+$		13.87			12.17	12.45
a $^3\Pi$	6.32	6.02	6.1[d]		6.58	
c $^3\Pi$	11.55	11.55			11.14	
(3) $^3\Pi$		11.82			12.17	
(4) $^3\Pi$		13.07			12.42	
(5) $^3\Pi$		13.64			12.77	

[a] Tilford and Simmons (1972).

[b] Nieslen *et al* (1980).

[c] Cooper and Kirby (1987).

[d] Cooper and Langhoff (1981).

[e] Chantranupong *et al* (1992).

[f] This work, valence CAS target.

[g] 11-state model for $^1\Sigma^+$, 12-state model for $^1\Pi$, 11-state model for $^3\Sigma^+$ and 13-state model for $^3\Pi$.

[h] This work, valence CAS + SD, model b.

experimental results for this series show a particular lack of smoothness, however.

The variation in our quantum defects is somewhat smoother than most of those obtained experimentally. Given the level of agreement between the various experiments, and the various perturbations (Eikema *et al* 1994) that need to be considered when interpreting experimental spectra, it is likely that this lack of smoothness may well be dependent on the details of the various models used to fit the experimental data.

There are two possible causes for our systematic underestimate of the quantum defect: neglect of nuclear motion effects in the calculation and inclusion of insufficient target polarization effects. It is unlikely that nuclear motion effects can account for the discrepancies because, in the absence of large perturbations, the quantum defects are observed to vary only weakly ($\leqslant$ 0.002) with vibrational quantum number. Similarly, recent calculations on NO by Rabadán and Tennyson (1997) found only slow dependence on internuclear separation except in the one case where there was an avoided crossing. Conversely the CAS + SD calculations give quantum defects which are lower than the valence CAS ones by up to 0.01. As the CAS + SD model is some way off a fully correlated (polarized) model, this is the aspect of the calculation which must be improved if accurate quantum defects are required.

Table 6. Quantum defects of the singlet states of CO. Experimental values are for the ground vibrational level the electronic state; theoretical values are for a fixed bond length of 2.132 a_0.

	Experiment				Theory		
	a	b	c	d	e	f, g	h, g
3sσ B $^1\Sigma^+$	0.95		0.950		1.084	0.888	0.893
4sσ J $^1\Sigma^+$	0.92	0.921	0.921	0.920	1.054	0.857	0.864
5sσ I$'$ $^1\Sigma^+$			0.943	0.934	1.043	0.849	0.857
6sσ $^1\Sigma^+$			0.913	0.908	1.035	0.846	0.854
7sσ $^1\Sigma^+$				0.928	1.035	0.844	0.853
3pσ C $^1\Sigma^+$	0.72	0.720	0.720		0.684	0.665	0.674
4pσ K $^1\Sigma^+$	0.67	0.683	0.683		0.666	0.634	0.642
5pσ $^1\Sigma^+$		0.675	0.671	0.669	0.657	0.623	0.631
6pσ $^1\Sigma^+$		0.658	0.666	0.663	0.653	0.618	0.626
7pσ $^1\Sigma^+$		0.647		0.656	0.650	0.615	0.623
3dσ F $^1\Sigma^+$	0.13	0.127	0.126		0.014	0.044	0.048
4dσ $^1\Sigma^+$	0.14		0.137		0.013	0.050	0.056
5dσ $^1\Sigma^+$	0.15		0.146		0.030	0.052	0.060
4fσ $^1\Sigma^+$				0.017		0.009	0.009
5fσ $^1\Sigma^+$				0.020		0.010	0.010
6fσ $^1\Sigma^+$				0.020		0.010	0.010
3pπ E $^1\Pi$	0.66	0.663	0.664		0.656	0.589	0.596
4pπ L $^1\Pi$	0.67	0.647	0.646		0.623	0.588	0.595
5pπ $^1\Pi$		0.656	0.595	0.582 0.608	0.610	0.587	0.594
6pπ $^1\Pi$		0.644	0.645	0.638	0.604	0.586	0.595
7pπ $^1\Pi$		0.622		0.595	0.598	0.586	0.596
3dπ G $^1\Pi$	−0.03	−0.024	−0.024		0.019	−0.063	−0.058

[a] Hammond *et al* (1985).
[b] Ogawa and Ogawa (1972, 1974).
[c] Eidelsberg and Rostas (1990).
[d] Komatsu *et al* (1995)
[e] Singleton *et al* (1995)
[f] This work, valence CAS target.
[g] 11-state model for $^1\Sigma^+$, 12-state model for $^1\Pi$.
[h] This work, valence CAS + SD, model b.

3.3. Comparison with previous results: triplet states

There is very much less published data to compare with for CO triplet states. In particular there appears to have been no attempt to treat these *ab initio* since Cooper and Langhoff (1981), who considered several singlets but only the a $^3\Pi$ state. This situation should be contrasted with recent high-level studies of the quintet states (e.g. Bauschlicher *et al* 1993).

In contrast to the A $^1\Pi$ state discussed above, our X $^1\Sigma^+ \rightarrow$ a $^3\Pi$ excitation energy is in reasonable agreement with experiment; the difficulty of representing the A $^1\Pi$ and a $^3\Pi$ valence states within a common orbital basis set has been noted before (Morgan and Tennyson 1993). The excitation energy to the other triplet valence state, a$'$ $^3\Sigma^+$ appears to be seriously overestimated.

Table 7. Quantum defects of the triplet states of CO. Experimental values are for the ground vibrational level the electronic state; theoretical values are for a fixed bond length of 2.132 a_0.

	Experiment			Theory	
	a	b	c	d, e	f, e
3sσ b $^3\Sigma^+$	1.06			1.004	1.012
4sσ h $^3\Sigma^+$	1.05	1.053		0.934	0.938
3pσ j $^3\Sigma^+$	0.77		0.776	0.704	0.711
4pσ $^3\Sigma^+$			0.737	0.673	0.679
5pσ $^3\Sigma^+$			0.723	0.662	0.668
6pσ $^3\Sigma^+$			0.714	0.656	0.663
7pσ $^3\Sigma^+$			0.710	0.653	0.660
3dσ g $^3\Sigma^+$	0.15		0.161	0.094	0.093
4dσ $^3\Sigma^+$	0.14		0.161	0.102	0.125
5dσ $^3\Sigma^+$	0.15			0.105	0.103
3pπ c $^3\Pi$	0.71		0.711	0.667	
4pπ $^3\Pi$			0.655	0.637	
5pπ $^3\Pi$			0.658	0.630	
6pπ $^3\Pi$			0.651	0.626	

[a] Hammond *et al* (1985).

[b] Ogawa and Ogawa (1974), their reported 3dσ g $^3\Sigma^+$ observation has since been re-assigned to a vibrationally excited state of the 3pσ $^1\Sigma^+$state by Eidelsberg and Rostas (1990).

[c] Mellinger and Vidal (1995) and Mellinger *et al* (1996).

[d] This work, valence CAS target.

[e] 11-state model for $^3\Sigma^+$ and 13-state model for $^3\Pi$.

[f] This work, valence CAS + SD, model b.

Table 7 gives a comparison of quantum defects for the triplet Rydberg states. There appear to be no other *ab initio* calculations of these quantum defects. As for the singlets, the experimental (vibrational ground state) quantum defects are systematically higher than those obtained here. The differences are generally 0.07 or less, somewhat less than was found for the singlets. Again the CAS + SD quantum defects are generally larger. In most cases the limited trends observable in the experimental dataset are well reproduced.

The relatively large error in the quantum defects of up to 0.08 for the singlets and 0.07 for the triplets for the valence CAS calculation is at first sight surprising given that Rabadán and Tennyson (1996) obtained errors of only 0.06 for their NO quantum defects. Their calculation was similar in spirit to the present ones but used targets based on a more limited valence CAS wavefunction and only a 4-state close-coupling expansion. Subsequent calculations using a model more equivalent to the one used here (Rabadán and Tennyson 1997) significantly reduce this error. However NO$^+$ is a closed-shell target and its Rydberg states are probably not as sensitive to target polarization effects as the open-shell CO$^+$ system.

Table 7 does not present results for quantum defects of $^3\Pi$ states computed within the CAS + SD model. The reason for this is computational. This 13-state calculation requires 57 547 CSFs to construct a full matrix of dimension 1235 647, which is never explicitly generated in SCATCI (Tennyson 1996a), and which in turn gives a final matrix of dimension 12 248. The largest calculation successfully completed here was for the 11-state CAS + SD $^1\Pi$ model which used 33 767 prototype CSFs, a full matrix of 717 626 and a final matrix of dimension 7797. This calculation used 36 h CPU time on a single process of a DEC alpha 8400 workstation. Over 80% of this time was spent obtaining all the eigenvalues and eigenvectors of the final matrix. One can estimate that the corresponding $^3\Pi$ calculation would take six days and it was not attempted. In both these cases the dimension of the final matrix is dominated by the number of orthogonality relaxing CSFs.

4. Conclusions

Bound-state calculations for valence and Rydberg states of CO have been performed using an R-matrix based scattering procedure. These calculations give reasonable results for the whole range of CO bound electronic states. There are two areas which would seem ripe for improvement. The first is the representation of the target wavefunctions. Calculations performed using CAS wavefunctions gave good results, which were improved by the addition of single and double excitations to the target wavefunctions. Extension of the CAS + SD model to use a more realistic space for the double excitations will necessarily lead to a huge increase in the number of orthogonality relaxing configurations used in the calculation and hence in the size of the final matrix. It is clear that under these circumstances complete direct diagonalization of this matrix will no longer be practical and other approaches (see Pfingst *et al* 1994 for example) will have to be employed.

The second area which needs attention is the close-coupling expansions used to introduce target polarization effects into the calculation. How to optimize these expansions for the case of complex (many electron) targets is the subject of considerable study for electron–atom, atomic ion calculations. It would seem timely to address this problem for molecular systems too.

Finally it should be noted that several of the excited target states included in the close-coupling expansion are reasonable representations of the excited states of CO^+. Many of the experimental studies quoted above studied the behaviour of CO Rydberg series, both bound and autoionizing, associated with these excited electronic states. It would be a straightforward matter to extend the present calculations to consider these states, or indeed other aspects of electron–CO^+ physics including photoionization, electron impact excitation or, with nuclear motion, dissociative recombination.

Acknowledgments

I thank Kate Kirby and Lesley Morgan for many helpful discussions, and Ismanuel Rabadán for help with performing the CO bound state calculations and his comments on this manuscript. I also thank the members of ITAMP and JILA for their hospitality during my sabbatical when this work was performed. This work was supported by the UK Engineering and Physical Sciences Research Council under grants GR/K47702 and GR/K89214, and the National Science Foundation through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and the Smithsonian Astrophysical Observatory.

References

Andersson K, Malmqvist P-Å, Roos B J, Sadlej A J and Wolinski K 1990 *J. Chem. Phys.* **94** 5483–8
Baker J, Tchang-Brillet W-Ü L and Julienne P S 1995 *J. Chem. Phys.* **102** 3956–61
Baltzer P, Lundqvist M, Wannberg B, Karlson L, Larsson M, Hayes M A, West J B, Siggel M R F, Parr A C and Dehmer J L 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 4915–32
Bauschlicher C W Jr, Langhoff S R and Partridge H 1993 *J. Chem. Phys.* **98** 8785–9
Branchett S E and Tennyson J 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 2017–26
Bray I and Stelbovics A T 1995 *Adv. At. Mol. Opt. Phys.* **35** 210–54
Buttle P J A 1967 *Phys. Rev.* **160** 719–29

Chantranupong L, Bhanprakash K, Honigmann M, Hirsch G and Buenker R J 1992 *Chem. Phys.* **161** 351–62

Cooper D M and Langhoff S R 1981 *J. Chem. Phys.* **74** 1200–10

Cooper D L and Kirby K 1987 *J. Chem. Phys.* **87** 424–32

——1988 *Chem. Phys. Lett.* **152** 393–6

Cosby P C 1993 *J. Chem. Phys.* **98** 7804–18

Dadouch A, Dujardin G, Hellner L, Besnard-Ramage M J and Olsson B J 1991 *Phys. Rev.* A **43** 6057–65

Drabbels M, Heinze J, ter Meulen J J and Meerts W L 1993 *J. Chem. Phys.* **99** 5701–10

Eidelsberg M and Rostas F 1990 *Astron. Astrophys.* **235** 472–89

Eikema K S E, Hogervorst W and Ubrachs W 1994 *Chem. Phys.* **181** 217–45

Ebata T, Hosoi N and Ito M 1992 *J. Chem. Phys.* **97** 3920–30

Ebata T, Sutani T and Mikami N 1995 *Chem. Phys. Lett.* **240** 357–61

Gillan C J, Tennyson J and Burke P G 1995 *Computational Methods for Electron–Molecule Collisions* ed W M Huo and F A Gianturco (New York: Plenum)

Gillan C J, Tennyson J, McLaughlin B M and Burke P G, 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 1525–30

Hammond P, King G C, Jureta J and Read F H 1985 *J. Phys. B: At. Mol. Phys.* **18** 2057–73

Hardis J E, Ferrett T A, Southworth S H, Parr A C, Roy P, Dehmer J L, Dehmer P M and Chupka W A 1988 *J. Chem. Phys.* **89** 812–9

Huber K P and Herzberg G 1979 *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)

Kaufmann K 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 2277–94

Kirby K and Cooper D L 1989 *J. Chem. Phys.* **90** 4895–902

Kirby K, Rosenkrantz M E and Cooper D L 1992 *Phys. Rev. Lett.* **68** 3865–8

Kirby-Docken K and Liu B 1977 *J. Chem. Phys.* **66** 4309

Komatsu M, Ebata T, Maeyama T and Mikami N 1995 *J. Chem. Phys.* **103** 2420–35

Langhoff P W, Langhoff S R, Rescigno T N, Schrimer J, Cederbaum L S, Domcke W and Von Niessen W 1981 *Chem. Phys.* **58** 71–91

Lavendy H, Robbe J M and Flament J P 1993 *Chem. Phys. Lett.* **205** 456–60

Lefebvre-Brion H, Moser C M and Nesbet R K 1964 *J. Mol. Spectrosc.* **13** 418–29

Lescop B, Benarfa M, Lecoz G, Cherid M, Sinou G, Lenadan A and Tuffin F 1996 *Chem. Phys. Lett.* **252** 327–32

Leyh B and Raseev G 1986 *Phys. Rev.* A **34** 2920–35

——1988 *J. Chem. Phys.* **89** 820–9

Martin P A and Fehér M 1995 *Chem. Phys. Lett.* **232** 491–6

Masaki T, Adachi Y and Hirose C 1995 *Chem. Phys. Lett.* **139** 62–5

McLean A D 1971 *Conf. Potential Energy Surfaces in Chemistry* ed W A Lester Jr (San Jose, CA: IBM Research Laboratory) p 87

Mellinger A and Vidal C R 1995 *Chem. Phys. Lett.* **238** 31–6

Mellinger A, Vidal C R and Jungen C 1996 *J. Chem. Phys.* **104** 8913–21

Morgan L A and Tennyson J 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 2429–41

Nielsen E S, Jorgensen P and Oddershede J 1980 *J. Chem. Phys.* **73** 6238–46

Noble C J and Nesbet R K 1984 *Comput. Phys. Commun.* **33** 399

Ogawa M and Ogawa S 1972 *J. Mol. Spectrosc.* **41** 393–408

Ogawa S and Ogawa M 1974 *J. Mol. Spectrosc.* **49** 454–60

Opacity Project Team 1995 *The Opacity Project I* (Bristol: IOP)

Pfingst K, Nestman B M and Peyerimhoff S D 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 2283–96

Rabadán I and Tennyson J 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 3747–61

——1997 *J. Phys. B: At. Mol. Opt. Phys.* submitted

Rescigno T N 1994 *Phys. Rev.* A **50** 1382–9

Rosenkrantz M E and Kirby K 1989 *J. Chem. Phys.* **87** 6528–32

Salvini S A, Burke P G and Noble C J 1984 *J. Phys. B: At. Mol. Phys.* **17** 2549–61

Sarpal B K, Branchett S E, Tennyson J and Morgan L A 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 3685–99

Singleton L, Brint P and Thomas G P 1995 *J. Chem. Soc. Faraday Trans.* **91** 2699–707

Stathopoulos A and Froese Fischer C 1994 *Comput. Phys. Commun.* **79** 268–90

Tennyson J 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 805–16

——1996a *J. Phys. B: At. Mol. Opt. Phys.* **29** 1817–28

——1996b *Comput. Phys. Commun.* in press

Tennyson J, Burke P G and Berrington K A 1987 *Comput. Phys. Commun.* **47** 207–12

Tilford S G and Simmons J D 1972 *J. Phys. Chem. Data* **1** 147–87

Zobel J, Mayer U, Jung K, Ehrhardt H, Pritchard H, Winstead C and McKoy 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 839–56