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Ab initio computation of the interaction energy curves for some low-lying states of CO which dissociate to ground-state ^3P O and ^3P C atoms

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Summary. We investigate the molecular electronic structure of the quintet states of CO which correspond to the C(^3P) + O(^3P) interaction at several levels of theory. We find the 1 $^5\Sigma^+$ state to be relatively deeply bound (D_e ca. 587 cm^{-1}) while the other quintets have relatively shallow potential wells ($D_e < 40$ cm^{-1}) according to our multireference configuration interaction calculations which are counterpoise corrected for basis set superposition effects. Our results are in qualitative accord with the recent semiempirical estimates of Bussery and coworkers [(1989) Chem. Phys. 134:7].

Key words: Carbon monoxide quintet states – Long-range interactions – Electronic structure – Multireference configuration interaction

1. Introduction

Of the 18 states which result from the interaction $^3P_J\mathrm{C} + {}^3P_J\mathrm{O}$ according to Hund's coupling case a, there are two Σ^+, two Π, one Σ^- and one Δ state for each of the singlet, triplet and quintet spin multiplicities. While work continues to characterize the singlets and triplets of CO both experimentally and theoretically [1], very little is known about the quintets which correspond asymptotically to the interaction of ground state C and O atoms.

The pioneering quantum-mechanical investigation of O'Neil and Schaefer (ONS) [1] provides the only *ab initio* treatment of the quintets of CO. In a full configuration interaction treatment which utilized a minimal basis set they found the 1 $^5\Pi$ and 1 $^5\Sigma^+$ states to be fairly strongly bound; $D_e(1\ {}^5\Pi) = 3500$ cm^{-1} and $D_e(1\ {}^5\Sigma^+) = 3200$ cm^{-1}. The other four quintet potentials were repulsive in the range of internuclear separations ($R \leqslant 5\ a_0$) treated by them. One may infer from the ONS work that, if they are bound at all, the remaining quintets have minima

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which lie at separations larger than 5 a_0. However, it seems unlikely that the 1 $^5\Pi$ state should be so deeply bound in view of an analysis of the long range interaction region.

Recently, Bussery and co-workers (BRKAF) [3] published a semiempirical treatment of the long range interaction of ground state ^3P carbon and oxygen atoms where overlap effects are assumed to be negligible. They suggest that the 1 $^5\Sigma^+$ state is by far the most strongly bound of these quintets, due mainly to the attractive interaction of the atomic quadrupoles and that the 2 $^5\Pi$ state is repulsive. Further, they suggest that the 2 $^5\Sigma^+$, 1 $^5\Sigma^-$ and 1 $^5\Pi$ states are bound only by relatively weak dispersion interactions supplemented by a weak quadrupole-quadrupole attraction in the case of the Δ state. Unfortunately, the BRKAF treatment is not valid for internuclear separations $R < 7\, a_0$, while the ONS calculations did not extend beyond $R = 5\, a_0$.

It is our purpose to perform *ab initio* calculations not only to fill the gap between the limits of validity on the ONS and BRKAF treatments, but also to overlap each of them sufficiently to be able to shed some further light on the interaction energies of CO quintets over a useful range of internuclear separations.

Since we expect the dispersion terms to make an important contribution to the binding energies [4], we take particular care to optimize the basis set for each atom for their dipole, quadrupole and octupole polarizabilities as we report in Sect. 2. This makes it possible for a configuration interaction treatment which contains "split-single" excitations to reproduce the conventional multipole expansion of the interaction energy through terms $C_{10}R^{-10}$. We outline the molecular structure computations in Sect. 3 including our attempts to mitigate the size consistency problem and basis set superposition effects, and discuss the results in Sect. 4. There we show that the 1 $^5\Sigma^+$ state of CO is by far the most deeply bound of the quintets corresponding to the interaction of ground-state carbon and oxygen atoms. In general, we agree reasonably well with the results of BRKAF but not with those of ONS.

2. Basis set development

Recall that it is our goal to obtain accurate potential energy curves for the quintet states of CO which correspond asymptotically to the interaction of C(^3P) and O(^3P). Since we presume these molecular states to be weakly bound van der Waals states, it is doubly important that the basis sets for these calculations be carefully chosen.

For both atoms we began with the 15 function Slater basis sets of McLean and Liu [5] (ML) which are given in Table 1. The starting bases were augmented by a Rydberg 3*s* and a Rydberg 3*p* function (so that all the molecular calculations will have orbitals with some Rydberg character). We discuss the optimization procedure we employed later. We further augmented and/or changed the basis to include polarization functions. The latter are necessary to account for the polarization of an atom's charge distribution when another atom or a molecule is brought near it. These polarization effects are the driving forces behind the formation of van der Waals molecules. For each atom, we re-optimized the most diffuse 3*d* function of the original ML bases for the dipole polarizability; we optimized an added 4*f* function for the quadrupole polarizability and we optimized an added 5*g* function for the octupole polarizability.

Table 1. The Slater basis set for C and O

a. The original McLean and Liu [5] 6*s*, 4*p*, 3*d*, 2*f* basis

seq #	*n*	*l*	ζ values	
			carbon	oxygen
1	1	0	9.4826	13.7574
2	1	0	5.4360	7.6141
3	2	0	4.2010	5.8660
4	2	0	2.6844	4.3120
5	2	0	1.5243	2.4802
6	2	0	1.0575	1.6982
8	2	1	6.5100	7.5648
9	2	1	2.6005	3.4499
10	2	1	1.4436	1.8173
11	2	1	0.9807	1.1439
13	3	2	3.6407	4.8299
14	3	2	2.0211	2.5442
15	3	2	1.3730	1.6015
16	4	3	2.5985	3.2711
17	4	3	1.7653	2.0590

b. Rydberg and polarizing functions. The sequence numbers indicate where these functions belong in the basis set of section a, above

7	3	0	0.60186	0.70536
12	3	1	0.48707	0.54074
15[a]	3	2	0.87500	1.24837
18	4	3	0.92500	1.18750
19	5	4	0.94375	1.16250

[a] This replaces basis function # 15 from the original McLean and Liu basis

Furthermore, we performed a test for the carbon atom to see if adding a *p* function improved the quadrupole polarizability. It did not. In a similar test we added a *d* function to see if the octupole polarizability was changed significantly by its addition. The octupole polarizability of C was changed by about 3% (from 699 a_0 to 719 a_0) by adding a 3*d* function. This was not deemed a large enough change to include it in an already very large basis. However, it indicates that the error in the octupole polarizability is relatively small. The additions and changes to the ML basis are given in Table 1.

A few words about the optimization procedure are in order. We used the ALCHEMY [6] system's Slater integrals and SCF programs to optimize (i.e., minimize) the energy of Rydberg states of the atoms. For carbon, this was done by minimizing the energy with respect to the added functions of the triplet *P* states with the following electron configurations: $1s\sigma^2\,2p\sigma\,3s\sigma^2\,2p\pi$ (to obtain the 3*s* functions) and $1s\sigma^2\,2s\sigma^2\,2p\sigma\,3p\pi$ (to obtain the 3*p* functions). It should be noted that these are not the lowest energy states of carbon containing 3*s* and 3*p* orbitals. However, in a single configuration calculation the 2*s*(2*p*) orbitals have to be removed to prevent orbital degeneracies from occurring. For oxygen, we added the 3*s* and 3*p* functions and optimized the SCF energy of the quintet *S* and *P* states.

To obtain the dipole, quadrupole and octupole polarizabilities, we used the ATMBIS SCF program of A. C. Wahl as amended by W. J. Stevens [7] to include the finite field approximation [8]. The added (or changed) functions were chosen to maximize the energy difference between the field "on" and the field "off" cases. The maximization process always took place with the function to be added present in either the sigma space (denoted by $M_\ell = 0$) or else only in the pi orbital space (denoted by $M_\ell = 1$) (except, of course, for the optimization of the 3*s* function). We determined the final values of the polarizabilities with the optimized functions present in all the appropriate orbital spaces. The polarizabilities we obtained are given in Table 2. There we show that both the sigma ($M_\ell = 0$) and pi ($M_\ell = 1$) projections of the polarizabilities, and consequently, the average value ($\bar{\alpha}$) and the anisotropy (γ) agree nicely with the carefully optimized values of Meyer and co-workers [9, 10]. The energies we calculated with these basis sets are given in Table 3. There we show that the atomic excitation energy values (ΔE) which we calculate agree reasonably well with experiment [11].

Table 2. Dipole, quadrupole, and octupole polarizabilities of C and O in atomic units

			ML basis	Present	Meyer et al.[a]
C	α_d	$M_\ell = 0$		10.102	10.10
	α_d	1	12.362	12.990	13.05
	α_d			12.027	12.07
	γ_d			2.888	2.95
	α_q	$M_\ell = 0$		41.60	41.73
	α_q	1	46.49	61.80	61.28
	α_q			55.07	54.76
	γ_q			20.20	19.55
	α_0	$M_\ell = 0$		449.57	
	α_0	1	253.18	697.73	
	$\bar{\alpha}_0$			615.01	
	γ_0			248.16	
O	α_d	$M_\ell = 0$		5.005	5.14
	α_d	1	4.23	4.540	4.58
	$\bar{\alpha}_d$			4.695	4.77
	γ_d			−0.465	−0.56
	α_q	$M_\ell = 0$		20.32	20.61
	α_q	1	11.41	14.74	15.05
	$\bar{\alpha}_q$			16.60	16.90
	γ_q			−5.58	−5.56
	α_0	$M_\ell = 0$		141.542	
	α_0	1	37.33	98.352	
	$\bar{\alpha}_0$			112.749	
	γ_0			−43.190	

[a] Dipole polarizabilities from Ref. [9] quadrupole polarizabilities from Ref. [10]

Table 3. Atomic energies (in hartree atomic units) and excitation energies, ΔE, (in eV) for C and O atoms

Atom	State	$-$E(SCF)	$-$E(CI)	ΔE CI Calc	ΔE Expt[a]
C	^3P	37.6886303	37.7800911		
	^1D	.6315801	.7316137	1.32	1.26
	^1S	.5770546	.6819760	2.67	2.68
O	^3P	74.8102776	74.9767572		
	^1D	.7299571	.9032159	2.00	1.97
	^1S	.6507112	.8221247	4.21	4.19

[a] Values from Ref. [11]

3. MRCI calculations

Either a multi-configuration self consistent field (MCSCF) or a configuration interaction (CI) calculation is needed in order to obtain relatively reliable potential energy curves for the weakly interacting systems of interest here. At large internuclear separations the molecular orbitals are essentially atomic in nature. Thus, we can represent the electronic structure by the configuration $1s_{\mathrm{O}}^2\,1s_{\mathrm{C}}^2\,2s_{\mathrm{O}}^2\,2s_{\mathrm{C}}^2\,2p_{\mathrm{O}}^4\,2p_{\mathrm{C}}^2$, where we have written the atomic orbitals in the ascending order of the approximate energies of the atomic orbitals. Clearly, we must correlate all six of the valence level p electrons, and perhaps also correlate the carbon $2s$ electrons (for a total of eight). We deemed it to be too expensive to correlate the oxygen $2s$ electrons as well for a total of ten correlated electrons.

Since the treatment of the 1 $^5\Delta$ and 1 $^5\Sigma^-$ states is quite straightforward, let us discuss those calculations first. We use the output vectors from an SCF calculation for the 1 $^5\Sigma^+$ state as input to the valence MCSCF calculation with six active electrons distributed among two sigma and two pi orbitals. We call this a $(6e^-/2\sigma+2\pi)$ MC calculation. The MC computation for the $^5\Sigma^-$ state comprised four configuration state functions (CSF). We also correlated two more electrons in a $(8e^-/3\sigma+2\pi)$ MC calculation which comprised 21 CSF. We used the MC output as the input vectors for a second order CI(SOCI) calculation which comprised all single and double excitations of eight electrons from three σ and two π valence orbitals; we call these a $(8e^-/3\sigma+2\pi)$ CI computation. It comprised 386,389 CSF. The $(8e^-/3\sigma+2\pi)$ CI binding energies for the $^5\Sigma^-$ state were insensitive to whether we used the $(6e^-/2\sigma+2\pi)$ or the $(8e^-/3\sigma+2\pi)$ MC vectors as input. The results listed in Table 4 result from the $(8e^-/3\sigma+2\pi)$ SOCI based on $(8e^-/3\sigma+2\pi)$ MC vectors. The computations for the $^5\Delta$ state were quite similar to those for the $^5\Sigma^-$ state. The $^5\Delta$ results given in Table 4 correspond to an $(8e^-/3\sigma+2\pi)$ SOCI computation comprising 540,163 CSF and which itself is based on an $(8e^-/3\sigma+2\pi)$ MC computation comprising 15 CSF. (The SOCI computation step for each point required about 6 h of CPU time on an IBM 3090 computer.). The energies of the $^5\Sigma^-$ and $^5\Delta$ states are nearly degenerate at $R=30\,a_0$ as they should be.

The computations for the $^5\Sigma^+$ and $^5\Pi$ states were somewhat more involved since there are two states of each symmetry which correspond asymptotically to the interaction of ground-state C and O atoms. Let us consider the $^5\Sigma^+$ states. Neither the $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma^2\,1\pi^2\,2\pi^2$ configuration which is dominant at large

Table 4. Potential energies, in units of $-E_h$, of low lying quintet states of CO based on a $(8e^-/3\sigma + 2\pi)$ SOCI. These data are uncorrected for the basis set superposition effect

R (a_0)	$1\ ^5\Sigma^+$	$2\ ^5\Sigma^+$	$^5\Sigma^-$	$^2\Delta$
3.75	112.664062	112.619943		
4.0	112.667000	112.634461	112.631212	
4.1	112.667770	112.640298		
4.25	112.668556	112.646220		
4.5	112.669242	112.653411		
4.75	112.669439	112.658154		
5.0	112.669361	112.661231	112.660436	
5.25	112.669134	112.663194		
5.5	112.668837	112.664421	112.664146	
5.75	112.668517	112.665169		
6.0	112.668202	112.665609	112.665594	112.665850
6.25	112.667908	112.665855	112.665915	112.666124
6.5	112.667643	112.665981	112.666094	112.666265
6.75	112.667409	112.666033	112.666184	
7.0	112.667206	112.666042	112.666221	112.666338
7.2	112.667064	112.666033	112.666227	
7.5	112.666884	112.666001	112.666214	112.666297
8.0	112.666653	112.665934	112.666168	112.666228
9.0	112.666375	112.665816	112.666075	
10.0	112.666233	112.665741	112.666015	112.666034
12.0	112.666115	112.665669	112.665959	
20.0	112.666033	112.665616	112.665916	
30.0	112.666025	112.665611	112.665914	112.665912

separations for the 1 $^5\Sigma^+$ state nor the $1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma\, 6\sigma\, 1\pi^3\, 2\pi$ configuration which is dominant asymptotically for the 2 $^5\Sigma^+$ state corresponds asymptotically to ground-state carbon and oxygen atoms. However, a proper *average* of the two molecular configurations does correspond at long range to ground-state atoms. Thus, a mixture of one part of the 1 $^5\Sigma^+$ state wavefunction and two parts of the 2 $^5\Sigma^+$ state wavefunction corresponds at large separations to the wavefunction for ground state atoms. We ran a $(6e^-/2\sigma + 2\pi)$ state averaged MCSCF computation for the $^5\Sigma^+$ states with the weighting (1/3) 1 $^5\Sigma^+$ and (2/3) 2 $^5\Sigma^+$. At the internuclear separation $R = 30\, a_0$ we found the two $^5\Sigma^+$ states to be essentially degenerate (the two states were separated by 0.028 cm^{-1}) as they should be. However, a $(6e^-/2\sigma + 2\pi)$ SOCI calculation at $R = 30\, a_0$ based on these state averaged (SA) $(6e^-/2\sigma + 2\pi)$ MC output vectors yielded two roots which were separated by 330.29 cm^{-1}. Obviously the energy lowering afforded by excitations to the virtual space is different (by about 330 cm^{-1}) for the lowest two $^5\Sigma^+$ states. Clearly, the 4σ ($2s_\text{C}$) orbital also needs to be correlated. We then performed a $(8e^-/3\sigma + 2\pi)$ SOCI based on the same $(6e^-/2\sigma + 2\pi)$ SAMC vectors and found that the energy separation between the two $^5\Sigma^+$ states was reduced to 90.58 cm^{-1} at $R = 30\, a_0$. Furthermore, the $R = 30\, a_0$ energies for the 1 $^5\Delta$ and 1 $^5\Sigma^-$ states fall within this 91 cm^{-1} gap. This $(8e^-/3\sigma + 2\pi)$ SOCI computation for the $^5\Sigma^+$ states comprised 384,539 CSF, while the $(6e^-/2\sigma + 2\pi)$ SOCI required 57,898 CSF. A SOCI which correlates all ten electrons of the valence shell (including the $2s_\text{O}$), would presumably decrease the asymptotic non-degeneracy even further. Since such a calculation would have required 1,648,672 CSF for the ${}^5\Sigma^+$ states, we did not carry it out. The results in Table 4 for the 1, 2 ${}^5\Sigma^+$ states correspond to a $(8e^-/3\sigma + 2\pi)$ SOCI based on $(6e^-/2\sigma + 2\pi)$ 1/3–2/3 SAMC vectors.

Note that the 90.58 cm^{-1} separation at $R = 30\ a_0$ between the two ${}^5\Sigma^+$ states is not due to the fact that the 1 ${}^5\Sigma^+$ state has a fairly large attractive quadrupole-quadrupole interaction component while the corresponding term for the 2 ${}^5\Sigma^+$ state is zero. By using the C_5 constants obtained by BRKAF [3], we calculate the difference in energy between these two states due to the quadrupole-quadrupole interaction energy to be only about 0.1 cm^{-1} at $R = 30\ a_0$.

The situation for the 1, 2 ${}^5\Pi$ states is even more complicated. An equal mix of the three configurations $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma\ 1\pi^3\,2\pi^2$, $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma^2\,6\sigma\ 1\pi^2\,2\pi$ and $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma\ 6\sigma\ 1\pi^3\,2\pi$ is needed in order to assure asymptotic dissociation to ground state atoms. Note that the first two configurations are obviously Π configurations while the last one corresponds to the second root of ${}^5\Sigma^+$ symmetry. The appropriately weighted $(6e^-/2\sigma + 2\pi)$ SAMC calculated at $R = 30\ a_0$ yields three roots which differ from each other by at most 0.231 cm^{-1}. However, we were unable to carry out the three-state SAMC for a range of internuclear separations. The difficulty was that the roots kept flipping from iteration to iteration and the procedure would not converge. Thus, we abandoned our study of the Π states.

4. Discussion of results

To make further comparisons between the various quintet states let us transform the absolute energies of Table 4 into the binding energies of Table 5 and distill from them the characteristic constants listed in Table 4. We obtain the binding energies listed in Table 5 and shown in Fig. 1 by arbitrarily taking the zero of energy *for each state* to be its molecular energy at $R = 30\ a_0$. We correct the binding energy curves for the basis set superposition effects (BSSE) by applying the counterpoise technique of Boys and Bernardi [12]. That is, we calculate the energy of each ground state atom in the presence of the other "ghost" atom

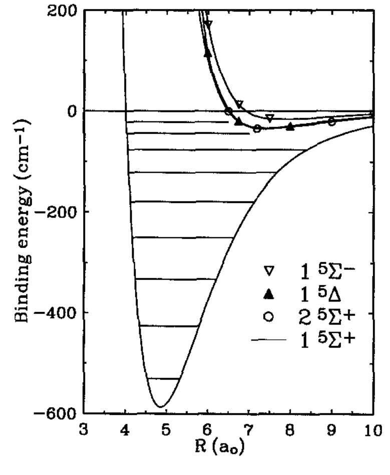

Fig. 1. The binding energy curves for low-lying quintet states of CO. The rotationless vibrational energy levels for the 1 ${}^5\Sigma^+$ state are depicted as *horizontal lines* extending between the classical turning points for $0 \leqslant v \leqslant 6$. The vibrational levels $7 \leqslant v \leqslant 8$ are terminated arbitrarily on the right so they do not overlap the plots of the weakly bound curves. The $v = 9$ and $V = 10$ levels are not drawn for the sake of clarity

Table 5. Binding energies (in cm^{-1}), which are counterpoise corrected for basis set superposition effects, of some quintet states of CO which correspond asymptotically to ground state carbon and oxygen atoms

R (a_0)	$1\ {}^5\Sigma^+$	$2\ {}^5\Sigma^+$	$1\ {}^5\Delta$	$1\ {}^5\Sigma^-$
3.75	+676.6	+10268.8		
4.0	+9.2	+7059.8		+7839.4
4.1	−168.3	+5770.3		
4.25	−352.9	+4458.4		
4.5	−521.1	+2861.7		
4.75	−582.1	+1803.8		
5.0	−580.2	+1113.3		+1354.3
5.25	−544.4	+668.4		
5.5	−492.4	+386.0		+512.8
5.75	−434.3	+209.6		
6.0	−376.6	+101.6	+114.8	+171.4
6.25	−322.6	+37.1	+44.2	+90.5
6.5	−274.1	−0.2	+3.5	+41.5
6.75	−231.6	−20.4		+12.9
7.0	−194.8	−30.2	−29.1	−3.0
7.2	−170.5	−34.9		−11.2
7.5	−137.8	−34.9	−33.8	−15.1
8.0	−97.9	−31.0	−29.5	−15.8
9.0	−53.0	−21.2		−11.5
10.0	−29.2	−12.0	−10.3	−5.7
12.0	−11.9	−4.8		−2.0
20.0	−1.3	−0.6		−0.0
30.0	0.0	0.0	0.0	0.0

[with zero charge on the "ghost" nucleus but with the full basis set] at each internuclear separation. The net effect of the counterpoise correction is to raise the binding energy curves at all separations to the left of the asymptotic point (which is taken to be 30.0 a_0). Consequently, the binding energy curves listed in Table 5 have minima which are shallower and which lie farther to the right than would curves uncorrected for BSSE.

For the resulting binding energies to be correct and for the corresponding potential curves to have the proper shapes, the correlation energies missing from our treatment would have to be independent of internuclear separation. There is no reason to believe that to be the case. Nevertheless, we expect that a fully correlated treatment would produce binding energy curves for the $1\ {}^5\Sigma^+$, $1\ {}^5\Delta$ and $1\ {}^5\Sigma^-$ states not too different from those listed in Table 6. Asymptotically the $2\ {}^5\Sigma^+$ curve must be lowered by about 90 cm^{-1} *more* than is the $1\ {}^5\Sigma^+$ curve. Thus, it may be somewhat less reliable than the other quintet binding energy curves. If the quadrupole-quadrupole coefficients of BRKAF [3] are an adequate guide, it appears that additional correlation would result in a $2\ {}^5\Sigma^+$ curve which is more nearly like the $1\ {}^5\Sigma^-$ curve than is suggested by the present results.

Our BSSE-corrected binding energy curves are in qualitative consonance with the long-range analysis of BRKAF [3] as shown in Fig. 2. The agreement between our binding energy curve for the relatively deeply bound $1\ {}^5\Sigma^+$ state and that obtained by BRKAF [3] is remarkable. The agreement is quite good all the

Table 6. Characteristic constants of low-lying quintet states of CO

	R_e, a_0	D_e, cm^{-1}	$\Delta G(1/2)$, cm^{-1}
$1\ {}^5\Sigma^+$	4.859	587.0	104.5
$2\ {}^5\Sigma^+$	7.327	35.7	15.2
$1\ {}^5\Delta$	7.425	34.0	17.2
$1\ {}^5\Sigma^-$	7.878	15.9	7.2

way down to about $R = 7\ a_0$, which is the lower limit of validity of the BRKAF long-range perturbation theory treatment according to the LeRoy [13] criterion. Clearly, the agreement between our present results, and those of BRKAF for the other quintets which are much more weakly bound is not nearly so good. The repulsions which ultimately cause the formation of minima in the potential curves are absent from the perturbation theory treatment. Thus, there is no hope for agreement between our own weakly bound potentials and the perturbation theory results at separations where the exchange repulsion comprises a significant part of the total energy of the system. Figure 2 suggests that this is true for separations as large as 10–12 a_0 for all but the $1\ {}^5\Sigma^+$ state. At least for the treatment of the present CO quintets the LeRoy lower limit should be increased by about 50%.

While we find the $1\ {}^5\Sigma^+$ state to be the most deeply bound of the quintets we consider, it is not nearly so deeply bound as was suggested by ONS [2] (who found $D_e = 3200\ \mathrm{cm}^{-1}$, $R_e = 3.59\ a_0$). We have repeated the ONS CI calculation for the $1\ {}^5\Sigma^+$ state and calculated the basis set superposition error according to the counterpoise scheme of Boys and Bernardi [12]. We find the ONS superposition error at $R = 4.0\ a_0$ to be about $2500\ \mathrm{cm}^{-1}$. This large error is not entirely unexpected since, of necessity, ONS were able to use only a minimal basis set in their early work.

It is clear from the present results that the $1\ {}^5\Sigma^+$ state of CO is sufficiently deeply bound to be thermally stable at reasonably low temperatures. Its dissociation energy of some $587\ \mathrm{cm}^{-1}$ (about 845 K) is about 3 kT at 0 °C and about

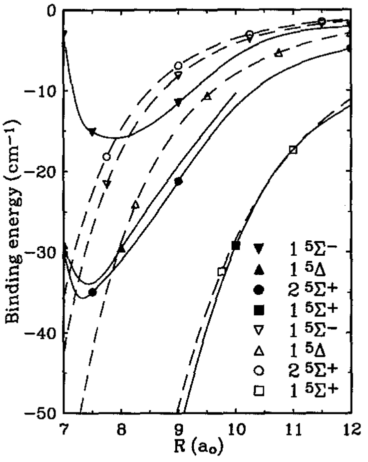

Fig. 2. Comparison of the long-range portions of our BSSE corrected curves (*solid lines* and *solid symbols*) with the perturbation theory results of BRKAF [3] (*dashed lines* and *unfilled symbols*)

Table 7. Vibrational energy levels, in cm^{-1}, for quintet states of CO

v	$1\,^5\Sigma^+$	$2\,^5\Sigma^+$	$1\,^5\Delta$	$1\,^5\Sigma^-$
0	56.4	12.3	13.0	8.0
1	160.9	27.5	30.2	15.2
2	254.6			
3	336.9			
4	407.3			
5	465.2			
6	510.6			
7	543.1			
8	565.4			
9	577.9			
10	584.0			

11 kT at 77 K. The $1\,^5\Sigma^+$ state has at least 11 bound vibrational energy levels, as we show in Table 7. Its fundamental frequency is sufficiently large ($\sim$150 K) so that thermal vibrational excitation would be a rare event at 77 K or below. The remaining quintet states have dissociation energies under 40 cm^{-1} ($\sim$60 K). Except for the $1\,^5\Sigma^+$ state the fundamental vibrational frequencies are all 25 K or below as is evident from the data in Table 7. This suggests a way to populate the $1\,^5\Sigma^+$ state selectively. If a mixture of ground-state carbon and oxygen atoms are kept at about 77 K in a magnetic field so that their spins are kept aligned, all quintets but the $1\,^5\Sigma^+$ state will be thermally unstable. Thus, any atom recombination will form the $1\,^5\Sigma^+$ state preferentially. There may, of course, be less subtle ways to form the CO quintets.

It remains to be learned the radiative lifetimes of the quintet states and to learn whether there are ways to control their various decay processes.

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In 1955 one of us (DDK) joined the research group of J. O. Hirschfelder at the University of Wisconsin. This was shortly after the publication in 1954 of that seminal work "Molecular Theory of Gases and Liquids" authored by Joe together with C. F. (Chuck) Curtiss and R. B. (Bob) Bird [4]. DDK's first research problem was to elucidate the long-range interaction of ground state oxygen (or of sulfur) atoms as a sum of their quadrupole-quadrupole and dispersion energies. It is fitting that we dedicate this paper on the low-lying quintet states of CO (whose asymptotic interaction energy comprises quadrupole-quadrupole and dispersion terms) to Joe's memory.

Whether we knew him personally as a friend and mentor or only as a towering figure in the literature of chemical physics, Joseph Oakland Hirschfelder has affected our professional – and perhaps even our personal – lives markedly. This influence persists even after Joe's death. We shall miss the opportunity to be invigorated by his infectious enthusiasm for the exploration of new ideas.

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Note added in proof

Bahrdt, Nahme and Schwentner [Chem. Phys. (1990) 144:273] have identified a metastable state of CO with a lifetime of about 1.5 ms which lies in the energy region 10.7 to 11.1 eV above the ground state. Based in part on our preliminary calculations, they have tentatively assigned it to the lowest $^5\Sigma^+$ state.