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Interaction between Lithium and Carbon Monoxide. 2. A Quantum Chemical Study of the Low Stoichiometry Complexes

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Abstract: A series of ab initio calculations have been performed in order to elucidate the electronic structure and the equilibrium geometry of the lithium carbonyl complexes observed in matrix isolation spectroscopy experiments. For the 1:1 complex (Li–CO), SCF and post SCF–CI calculations show that the stable (nondissociative) species corresponds to a linear $^2\Pi$ state in which the lithium atom faces the carbon end of the carbonyl group. An analogous $^2\Pi$ structure is also found for the linear 1:2 (OC–Li–CO) complex, while for the 2:1 (Li–CO–Li) complex two inequivalent linear geometries are found corresponding to $^1\Pi$ and $^3\Sigma$ states. In all these complexes large electron transfer toward the oxygen occurs, leading to large dipole moments for Li–CO and Li–CO–Li. The calculated force constants for the CO stretching are lowered considerably with respect to the value for free CO, explaining the large red shifts observed in the infrared spectra. A simple model of Li–CO interactions in the matrix as a charge-transfer complex between Li^+ and CO^- is presented. This model for this "intimate ion pair" interaction provides a unifying and simple interpretation of the calculated structures and a semiquantitative explanation for the observed infrared spectra.

(I) Introduction

In order to elucidate the nature of the specific interaction between alkali metal atoms and carbon monoxide, two complementary studies have been undertaken in this laboratory. One is an experimental approach based on matrix isolation spectroscopy of Li/CO mixtures trapped in krypton; the other is a theoretical approach based on ab initio calculations for some typical complexes involving at most three partners. The main results from these studies are presented in two papers. For the sake of clarity the first one[1] is devoted to the presentation of the experimental data and the second one (the present one) to the presentation of the quantum chemical calculations. The latter allows us to reach some fundamental conclusions about the nature of the interaction and the order of magnitude of the perturbation of the CO stretching vibrations, according to the nature of the aggregate. This information is of crucial importance in rationalizing the conclusions from the IR spectra at high Li concentrations, which are characterized by CO stretching modes spread over the whole spectral range from 1700 to 1000 cm^{-1} (paper I).[1]

The bonding of alkali atoms with carbon monoxide has been studied previously only for sodium, in order to interpret results from collision studies. The detailed calculations of Reiland et al.[2] and of Pacchioni[3] have shown that the structures are linear and that both the $^2\Sigma$ Na–CO and the $^2\Sigma$ Na–OC structures have a flat minimum in their potential curves at a value of the Na–CO distance of about 4 Å. These minima indicate that the complex is weakly bonded and stabilized by induction and dispersion forces. At this large value of the alkali–carbonyl distance, with bonding of this nature, there will not by any pronounced perturbation of the CO bond; therefore something else must be invoked in the case of the Li–CO complex to explain the large red shifts of the carbonyl stretching mode that have been observed experimentally.[1]

(II) Theoretical Problems and Technical Details

The main theoretical problem arising in the study of lithium complexes with carbon monoxide is the determination of the electronic structures and realistic prediction of equilibrium geometries for isolated typical $Li(CO)_x$ (with $x = 1$ or 2) complexes that model the species observed in a krypton matrix. It is reasonable to assume that the interactions between the LiCO compounds and the host rare gas matrix are not large enough to disturb either the ordering of the electronic states or the nuclear equilibrium configuration of the compound. However, it can be expected that species with large dipole moments will be stabilized by polarization of the matrix and even that a small alteration of the geometries from those for isolated molecules may occur along a soft coordinate if a large value is predicted for the dipole derivative with respect to the relevant coordinate. The solvation energy is difficult to evaluate since there is no well-founded quantitative theoretical procedure designed to do it accurately.

In the first step of the calculation, the energy hypersurface of the isolated complex was sampled at the unrestricted Hartree–Fock (UHF) level,[4] for complexes having open shells, using the standard 4-31G basis set of Ditchfield, Hehre, and Pople.[5] In the second step after minima are localized, a full optimization calculation was carried out by an analytic gradient procedure.[6] This geometry optimization was repeated with a 6-31G* basis set[7] in order to check the influence of polarization functions on the predicted structure. Finally the force constants are calculated (for both bases) by numerical differentiation of the forces, as originally proposed by Pulay.[8] All the SCF calculations have been performed with the MONSTERGAUSS program.[9] The CI calculations for the energy of the lowest electronic states of LiCO and of LiOC were performed for Li–C (or Li–O) distance ranging from 1.5 to 10 Å, from the SCF molecular orbitals for the $^2\Sigma$ states calculated at the restricted Hartree–Fock (RHF) level,[10] using a 4-31G basis set. For each symmetry up to 48 000 configurations were taken into account by the CIPSI program.[11,12]

(III) The 1:1 LiCO Complex

The 1:1 complex is identified in the spectrum[1] by two absorption bands whose intensity depends linearly on concentration. The stronger at 1806 cm^{-1} is assigned to the CO stretching vibration, while the weaker at 611 cm^{-1} corresponds to the LiC stretching vibration. The degenerate bending mode expected at still lower frequency has not been observed. The large red shift (about 340 cm^{-1}) of ν(CO) and the relatively high frequency (611 cm^{-1}) of ν(Li–CO) are not consistent with formation of a very weak

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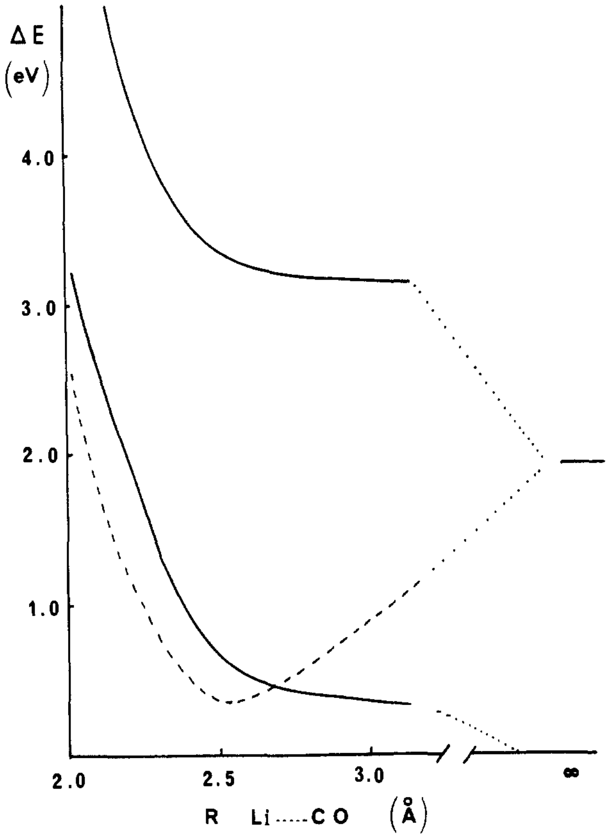

Figure 1. CI potential energy curves for the ground state and first excited states of LiCO in a colinear approach of Li to the carbon. The CO distance is fixed at the optimized UHF value of 1.173252 Å (—, $^2\Sigma$ states; ---, $^2\Pi$ state). The behavior at $R = \infty$ is an indicative extrapolation, and the energy scale is not absolute, but only indicative. Note that 1 eV = $0.0735E_H$ (or 96.48 kJ/mol).

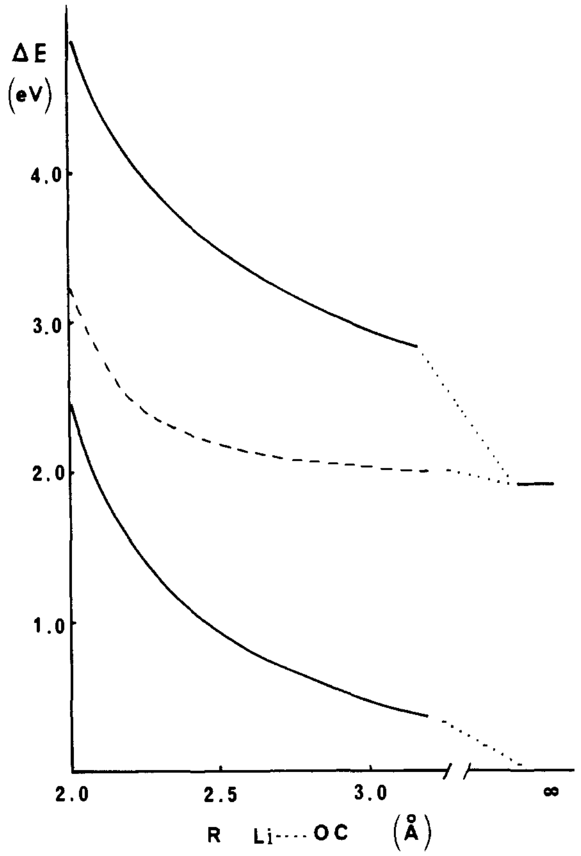

Figure 2. CI potential energy curves for the ground state and first excited states of LiOC in a colinear approach of Li to the oxygen atom. The CO distance is fixed at the optimized UHF value of 1.134254 Å (—, $^2\Sigma$; ---, $^2\Pi$ state). (See caption for Figure 1.)

complex as was predicted for the Na–CO system.[2,3]

The geometry optimization calculations carried out with both the 4-31G and the 6-31G* basis sets starting from several nonlinear configurations indicate that a minimum of the energy hypersurface exists for a linear Li--CO complex in the $^2\Pi$ state but that no minimum is found at Li–O distances less than 4.0 Å for the alternate Li--OC structure. In Figure 1 the potential energy curves for the two lowest $^2\Sigma$ states and for the lowest $^2\Pi$ state, all calculated at the CI level, are plotted as a function of the distance (separation) between the Li atom and the center of mass of the CO molecule for the Li--CO structure. Figure 2 shows the corresponding potential curves calculated at the CI level for the approach of lithium to the oxygen atom in the Li--OC structure. For the latter system no minimum is found for any electronic state shown. Note that all of the potential curves lie above the dissociation energy of the ground-state products [Li($^2S_{1/2}$) and CO($^1\Sigma^+$)] and that *only* the $^2\Pi$ state for the Li--CO structure is found to have an attractive potential. These CI results in Figures 1 and 2 are in agreement with the preliminary SCF results described above.

There are several points to be made in connection with the results shown in Figures 1 and 2. In the first place we note that the 1:1 LiCO complex is predicted to be unstable in the gas phase by $0.0166E_H$ (43.5 kJ/mol), with the 4-31G basis or by $0.0298E_H$ (78.1 kJ/mol) for the 6-31G* basis set. This prediction is somewhat misleading, in that it neglects both dispersion effects and the effect of the matrix, both of which are expected to stabilize the complex. Furthermore, the calculated results are not correct because of the neglect of basis set superposition error (BSSE).[13] We have estimated this correction to be $0.0022E_H$ at the 6-31G* level (at R = 2.0 Å) or $0.0044E_H$ with the 4-31G basis set so that this error accounts for a small portion of the difference in dissociation energies predicted for the complex using the two basis sets.[14]

The contribution of dispersion forces to the stability of the Li--CO complex is small and can be estimated to be only $-0.0073E_H$ (−19.1 kJ/mol) from an MP2/CI calculation performed with GAUSSIAN 80[15] using the 6-31G* basis set, so that the isolated gas-phase Li–CO complex in the $^2\Pi$ state is predicted to be metastable, with energy $0.024E_H$ (59.0 kJ/mole) above the dissociation limit. However, when this gas-phase complex is formed and trapped in a rare gas matrix, the large dipole moment of the complex may cause it to be stabilized by the polarization of the medium and the crystal field constraints.

Although these effects cannot be introduced in the rigorous calculations, we note that an induced reaction field of 0.24 V/Å is large enough to stabilize the complex. A crude Onsager model,[16] in which the impurity–matrix interaction is represented by the interaction between a point dipole at the center of a spherical cavity in a dielectric continuum, indicates that for Li–CO (μ = 5.11 D) in a krypton matrix (ϵ = 1.78) a reaction field of this size could be generated in a cavity with a diameter of 4.12 Å, which is approximately the size of a substitution site (4.02 Å) in the Kr lattice.[17] This stabilization could occur both for the $^2\Pi$ state and for the $^2\Sigma$ state. However, the latter $^2\Sigma$ potential curve would have only a broad shallow minimum with little effect on vibrational frequencies in contrast to the effects expected for the $^2\Pi$ state.

Hence, we believe that our calculation of the potential energy hypersurface for Li–CO summarized in Figures 1 and 2 indicates

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Table I. CO Monomer and Linear $^2\Pi$ 1:1 LiCO Complex: Optimized Geometries, CO Stretching Force Constants, Dipole Moments, and the Frequency Ratio of Complexed (ω) to Free (ω_0) CO Stretching Frequencies

		calculated		
		basis 4-31G	basis 6-31G*	exptl
CO	R(CO) (Å)	1.1277	1.1138	1.1283[a]
	k_r (mdyn Å^{-1})	21.5	24.04	19.02[b]
	μ (D)	0.60	0.26	−0.112[c]
Li CO	R(LiC) (Å)	1.8966	1.9306	
	R(CO) (Å)	1.1733	1.1436	
	K_R(CO) (mdyn Å^{-1})	14.00	16.08	13.2[d]
	μ (D)	6.66	5.11	
	$(K_R/k_r)^{1/2} \simeq \omega/\omega_0$	0.807	0.82	0.84[d]

[a] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979. [b] Calculated from ω_e = 2169.81 cm^{-1}. [c] Toth, R. A.; Hunt, R. H.; Plyler, E. K. *J. Mol. Spectrosc.* **1969**, *32*, 74. [d] Calculated from the uncorrected experimental frequencies of ref 1.

that only Li–CO (not Li–OC) is stable and that it exists in a linear arrangement probably in the $^2\Pi$ electronic state when the molecule trapped in a polarizable medium such as the krypton matrix. Although these arguments can be only semiquantitative at this stage, we believe the main features are significant.

For the lowest Na--CO and Na--OC $^2\Sigma$ states[2,3] the energy is found to be always lower than the energy of the $^2\Pi$ state, similar to the behavior shown here in Figure 2 for Li--OC and in contrast with the behavior predicted here for Li--CO. The difference in behavior predicted for Na--CO and for Li--CO is, we believe, due to two reasons: first, the energy difference between the ground $^2S_{1/2}$ state and the excited $^2P_{3/2}$ state is greater for Na than for Li, and second, the 3p orbitals are more extended in Na than are the 2p orbitals in Li, allowing closer approach of the Li to the carbon atom than is possible in Na--CO. It may be worth noting at this point that the shallowness of the drop in the energy of the $^2\Sigma$ states in Li--CO may be an indication of an approach to a shallow minimum at very long (~4 Å) Li--CO distances, but such an interaction could be much too weak to explain the spectrum observed for Li--CO in the matrix.

It is perhaps worth noting here that the calculated energy separation between the two $^2\Sigma$ states of Li–CO (and Li–OC) at R = 10Å is about 1.94 eV, corresponding to the experimental separation between $^2S_{1/2}$ and $^2P_{3/2}$ states of 1.85 eV for Li. This agreement is comparable to that calculated by Pachioni[3] for the corresponding separation in sodium (1.94 eV calculated and 2.10 eV experimental).

Vibrational Spectrum. Although the electronic structure of the LiCO complex is a fascinating subject and deserves further discussion, our purpose here is to consider the associated vibrational spectrum for this molecule. The optimized values computed at the SCF level for the bond distances for this $^2\Pi$ linear molecule, together with the C–O stretching force constants and dipole moments, are reported in Table I for the linear LiCO molecule and compared with the corresponding values for CO and with the relevant experimental data.

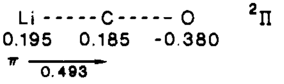
The ab initio calculation provides the Cartesian force constants and the dipole moment derivatives [atomic polar tensors[18]] in the Cartesian coordinates. From these values the frequencies and vibrational band intensities are obtained.[19] The results for LiCO are compared with the experimental observations[1] in Table II.

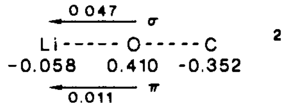
Usually the vibrational wavenumbers and intensities predicted in this kind of ab initio calculation made with a 4-31G basis set are in good [wavenumbers within 50 cm^{-1}; intensities to a "factor-of-two"[20]] agreement with the experimental values. Here (in Table II) we see that the predicted frequencies are in excellent agreement with the observed values. As usual, the calculated frequencies are somewhat higher than the experimental values, but the ratio ω/ω_0, predicted (Table I) for the frequency (ω) of CO in the complex to that for free CO (ω_0), is in very good agreement with experiment. The ratio of predicted intensities with the 4-31G basis appears to be in fair agreement with experiment, although the experimental value for the ratio $A_{\nu(CO)}/A_{\nu(LiC)}$ is about 10 compared to a predicted ratio of 100. The absolute magnitudes of the predicted intensities also appear to be fairly reasonable.

We have calculated the C–O force constants for different fixed Li–C distances in the Li--CO complex and also for an Li–O distance of 2.0 Å in the Li–OC complex. In all these calculations the C–O distance is reoptimized. For the calculations involving the Li–CO complex, the frequency ratio of complexed to free CO (ω/ω_0) is of the order of 0.8 when R(LiC) < 2.1 Å; at longer distances this ratio increases and ω/ω_0 = 1.0 at R(LiC) = 2.5 Å. On the other hand, ω/ω_0 = 1.0 even at this short Li–O distance (2.0 Å) in the Li--OC complex.

In summary, the $^2\Pi$ state of Li--CO is characterized by a large red shift in the C–O stretching vibration of the carbonyl, while the $^2\Sigma$ states of the same molecule, as well as all states of the Li--OC molecule, are characterized by frequencies that are almost unaffected by the process of complexation.

These differences can be understood in terms of the following diagrams, indicating the charge transfer for the $^2\Pi$ ground state of Li--CO compared with that for the $^2\Sigma$ ground state of Li--OC.





Here the numbers under the atoms give the Mulliken charges in e, while the numbers near the arrows give the number of electrons transferred from the σ and π systems, respectively, in the direction indicated by the arrows.

In the $^2\Pi$ state of LiCO, about 0.3 e is transferred from the σ system of CO to the Li atom, and 0.5 e is transferred from the Li atom to the antibonding π^* system of CO. The net charge transfer is substantial (0.2 e) but by no means complete. Both charge transfers weaken the CO bond and therefore have an additive effect on the red shift of the C–O stretching frequency in the $^2\Pi$ state. Conversely, for Li--OC, the extent of charge transfer is less by an order of magnitude so the resulting decrease in frequency of the C–O stretch is expected to be much smaller. These descriptions of the bonding in LiCO and in LiOC are very similar to those given by Blomberg et al. for Ni--CO and Ni--OH$_2$ complexes.[21]

(IV) The Li(CO)$_2$ 1:2 Complex

The 1:2 complex Li(CO)$_2$ gives rise to two pairs of C–O stretching bands in the spectrum, corresponding to two different trapping sites in the matrix.[1] In site I the antisymmetric CO stretching mode is located at 1712.5 cm^{-1} and the symmetric one at 1991 cm^{-1}, while in site II the corresponding bands are observed at 1721.5 and 1997.5 cm^{-1}, respectively. Assuming a C_{2v} structure of the complex, a Li–C–Li angle of 152° and 124° can be deduced from the intensity ratio $I_{\nu a}/I_{\nu s}$ for site I and II, respectively, if it is assumed (probably erroneously) that the dipole derivatives ($\partial\bar{\mu}/\partial r_1$ and $\partial\bar{\mu}/\partial r_2$) are oriented along the direction of the bonds. The geometry optimization carried out at the UHF level (4-31G and 4-31G* bases) predicts that the molecule is linear and symmetric ($D_{\infty h}$) in contradiction with experiment. However, the C–Li–C angle is a very "soft" coordinate so that distortion may occur in the matrix, helped by solvation energy due to a rather large dipole moment (about 1 D for ∠C–Li–C = 150°) in the C_{2v}

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[18] (a) Biarge, J. F.; Herranz, J.; Morcillo, J. *An. R. Soc. Esp. Fis. Quim. Ser. A*, **1961**, *57*, 81. (b) Person, W. B. In *Vibrational Intensities in Infrared and Raman Spectroscopy*; Person, W. B., Zerbi, G., Eds.; Elsevier: Amsterdam, 1982; Chapters 4 and 14.

[19] For example, see the description given by Latajka et al. (Latajka, Z.; Person, W. B.; Morokuma, K. *J. Mol. Structure* (*THEOCHEM*) **1986**, *135*, 253).

[20] For example, see the discussion of "factor-of-two" agreement: Chin, S.; Scott, I.; Szczepaniak, K.; Person, W. B. *J. Am. Chem. Soc.* **1984**, *106*, 3415.

Table II. Predicted and Observed Vibrational Wavenumbers and Intensities for the Linear $^2\Pi$ 1:1 LiCO Complex

	basis 4-31G		basis 6-31G*		
vibration	wavenumber (cm^{-1})	intensity, A (km mol^{-1})	wavenumber (cm^{-1})	intensity, A (km mol^{-1})	experiment[a]
ν(C=O) (σ)	1880.0	3298	1905.2	6045	1805 (strong)
ν(C—Li) (σ)	665.0	31.4	598.6	40.7	611 (weak)
δ(Li—C≡O) (π)	302.8	18.0	331.8	11.8	not observed

[a] Reference 1.

Table III. The Li(CO)$_2$ 1:2 Complex: Comparison of Calculated Optimized Structure and Carbonyl Stretching Force Constants with Observed Values

	calculated		
	basis 4-31G	basis 6-31G*	exptl[a]
R(Li-C) (Å)	2.0355	2.040	
R(C-O) (Å)	1.135	1.118	
θ(C-Li-C)	180°	180°	152° (124°)[b]
K_R(CO) (mdyn Å^{-1})	16.3	20.35	13.941 (14.066)[b]
$K_{rr'}$ (CO-CO) (mdyn Å^{-1})	3.45	1.95	2.071 (2.062)[b]

[a] From ref 1. [b] Experimental values for site **II**.

Table IV. The Linear 2:1 Li-CO-Li Complex: The Optimized Structures, Carbonyl Stretching Force Constants, CO Stretching Frequency Ratios, and Dipole Moments Calculated for the $^1\Pi$ and $^3\Sigma$ Electronic States

	basis 4-31G		basis 6-31G*	
	$^1\Pi$	$^3\Sigma$	$^1\Pi$	$^3\Sigma$
R(Li-C) (Å)	1.8334	1.8130	1.8483	1.8164
r(C-O) (Å)	1.2593	1.2962	1.2267	1.2628
R(O-Li) (Å)	1.6384	1.6121	1.6648	1.6352
K_R(CO) (mdyn Å^{-1})	9.262	7.804	10.664	8.377
ω/ω_0	0.656	0.587	0.666	0.590
μ (D)	5.46	3.04	6.29	4.04

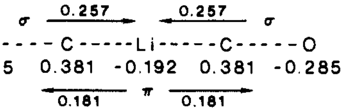
structure, and can reasonably explain an observed bent structure.

This disagreement between the experimental estimate of the C-Li-C angle and that from the ab initio calculations suggests that we should be skeptical about the predicted geometry. However, it is of some interest to examine the predicted vibrational spectrum for the linear OC--Li--CO molecule to see how well it agrees with the observed spectrum, realizing that we cannot totally disregard the possibility of other structures for which the SCF geometry optimization procedure does not converge.

For the linear OC--Li--CO molecule, the lowest electronic state is predicted to be a $^2\Pi_g$ state, consistent with the result for the Li--CO molecule. Addition of the second carbonyl to the Li--CO molecule is predicted (4-31G basis) to stabilize the system by $0.020E_H$ (52.7 kJ/mol) or $0.019E_H$ (50.2 kJ/mol) with a 6-31G* basis set. Therefore, the energy of this state of the complex at its minimum is predicted to be either $0.0035E_H$ (9.1 kJ/mol) below (4-31G basis) or $0.0107E_H$ (28.0 kJ/mol) above (6-31G* basis) the dissociation limit. The extra stabilization energy for the complex due to the dispersion forces is expected to be at least as large as for LiCO, so the isolated OC--Li--CO molecule is predicted to be stable, and the molecule in the matrix may be even more so. The predicted LiC and CO bond distances, the C-O stretching force constant, K_r, and the interaction constant K_{rr}, between the two C-O bonds are listed in Table III and compared there with the corresponding experimental values, where these are known.

These results compared with those in Table I show that the CO bond is predicted to be less perturbed in the 1:2 Li(CO)$_2$ complex than it is in the 1:1 LiCO complex. On the one hand, the Li-C distance in Li(CO)$_2$ is predicted to be 0.1 Å longer than in Li-CO. The CO bond distance in Li(CO)$_2$ is predicted to be only 0.0073 Å (4-31G basis) or 0.0042 Å (6-31G* basis) longer than in free CO, while in Li-CO the predicted increases for this bond were 0.043 and 0.03 Å, respectively. These results are consistent with the smaller perturbation of the CO bond in the 1:2 complex indicated also by the values of the diagonal C-O force constants given in Table III. Even so, a very large interaction force constant K_{rr}' (see Table III) is predicted for each basis set; the value from the 6-31G* basis is very close to the experimental value derived assuming that the molecule is bent in the matrix.

The electron transfers upon complexation are very similar to those found for the 1:1 complex (see below).



The σ charge transfer is of the same order as in the 1:1 complex, but the π back-donation of the 2p electrons toward CO is approximately three times smaller, resulting in a smaller decrease in CO force constant from that for the free molecule. The same difference is also found for the Ni(CO) and Ni(CO)$_2$ complexes[21] in their $^1\Sigma^+$ states, though such effects are less important in that case.

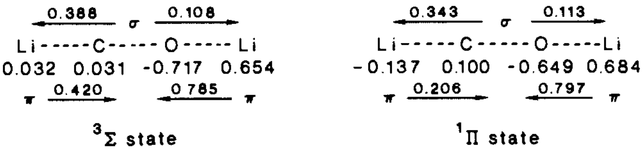
(V) The 2:1 Li$_2$CO Complex

The electronic state of the 2:1 Li$_2$CO complex can be either a singlet or a triplet. Several structures have been envisaged as the starting point for geometry optimization: the linear structures Li-Li-CO, Li-CO-Li; the T-shaped structures Li-Li-CO, CO-Li-Li; and the "flat-twin" side-on bonded Li-$^{\mathrm{C}}_{\mathrm{O}}$-Li structure. The optimization process did not converge for any of these except the linear Li-CO-Li structure. The values for the structural parameters and for the CO force constants obtained for the linear Li-CO-Li complex are reported in Table III. We realize that other structures for this complex cannot be ruled out even though the geometry optimization calculation did not converge.

The energy of the triplet state ($^3\Sigma$) is calculated to be $0.04E_H$ (105 kJ/mol) and $0.002E_H$ (5.2 kJ/mol) above the dissociation limit with use of the 6-31G* and 4-31G basis sets, respectively. This result is very similar to the one obtained for the 1:1 complex, and the same arguments invoked for the stabilization of the latter in the matrix are expected to hold for the 2:1 complex. The $^1\Pi$ state lies $0.04E_H$ (105 kJ/mol) above the triplet. Even though its dipole moment is larger than that for the $^3\Sigma$ state by 2 D, the presence of the complex in the $^1\Pi$ state in the matrix is highly improbable.

The structural parameters and C-O stretching force constants for the linear Li-OC-Li structure are reported in Table IV. The calculated C-O stretching force constant for the $^3\Sigma$ structure corresponds to a prediction that the CO frequency will be lowered to 1260 cm^{-1}. The absorption band located at 1596 cm^{-1} observed in the spectrum[1] has been tentatively assigned to the 2:1 complex on the grounds of isotopic effects.[1] The magnitude of the calculated red shift indicates that this conclusion is reasonable, especially since the calculation does not include environmental effects which might stabilize more than one conformation.

For this complex the electron transfers (in e) calculated from the Mulliken population analysis are given in the following sketch:



$^3\Sigma$ state $^1\Pi$ state

For both the $^3\Sigma$ and the $^1\Pi$ states a large transfer of π electronic

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(21) Blomberg, M. R. A.; Brandemark, U. B.; Siegbahn, P. E. M.; Mathisen, K. B.; Karlström, G. *J. Phys. Chem.* **1985**, *89*, 2171.

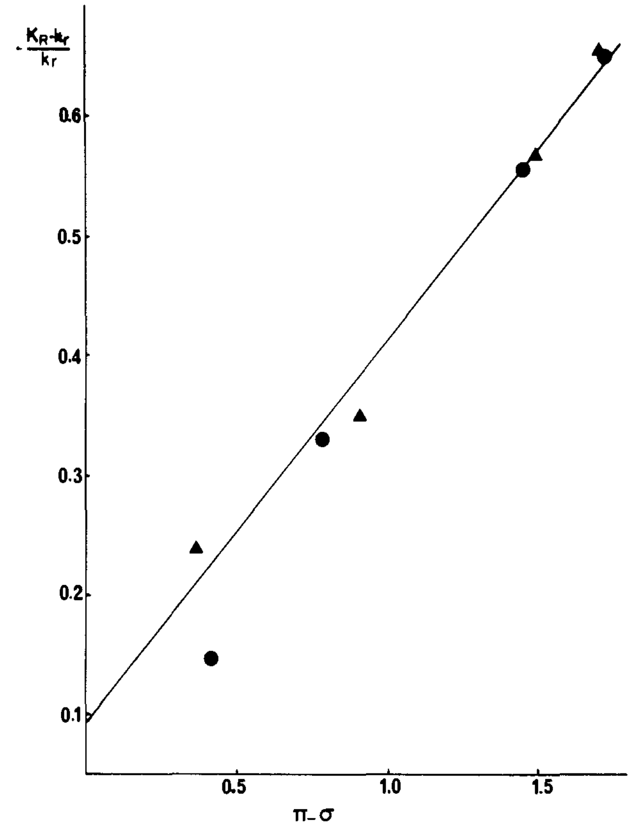

Figure 3. Normalized force constant lowering vs. effective charge transfer ($\pi - \sigma$) (▲, 4-31G; ●, 6-31G*).

charge is predicted from the lithium to the oxygen. The predicted σ transfer from oxygen toward lithium is rather small. On the other end of the molecule a σ transfer from carbon to lithium and a back-donation of π electrons is predicted; the magnitude of the π transfer on this side is two times larger for the $^2\Sigma$ than for the $^1\Pi$ state. All of these effects result in a very low value predicted for the C–O stretching force constant for the linear complex in the $^3\Sigma$ state.

(VI) Discussion

The bonding of lithium to carbon monoxide is characterized by an important decrease of the C–O force constant which reflects the lengthening of the CO bond and which has been explained by the simple electron transfer scheme. Although the σ and π electron transfers are directionally opposed, both of them contribute to weaken the CO bond.[22] It is then tempting to find empirical relations between the increase in CO bond length or in the variation of the C–O force constant and the magnitude of these transfers.

In Figures 3 and 4 the values of the normalized change in force constant $[(K_R - k_r)/k_r]$ and of the increase in C–O bond length (Δr) are plotted as a function of the electron transfer difference ($\pi - \sigma$) in e. Here K_R is the force constant of the C–O bond calculated for the C–O bond in the complexes, k_r is the value calculated for the free molecule, and Δr is the difference between R(C–O) in the complex and r(C–O) calculated for the free molecule. The π and σ transfers are defined to be positive when they occur from Li to the carbonyl. Their difference ($\pi - \sigma$) is a measure of the gross antibonding effect of the electron transfers. The figures show points calculated with the 4-31G basis set as well as those from the 6-31G* basis.

The lengthening of the C–O bond appears to be an almost linear function of the effective transfer ($\pi - \sigma$). The equation of the line is given approximately by

$$\Delta r \simeq -0.0502 + 0.117(\pi - \sigma) \qquad (1)$$

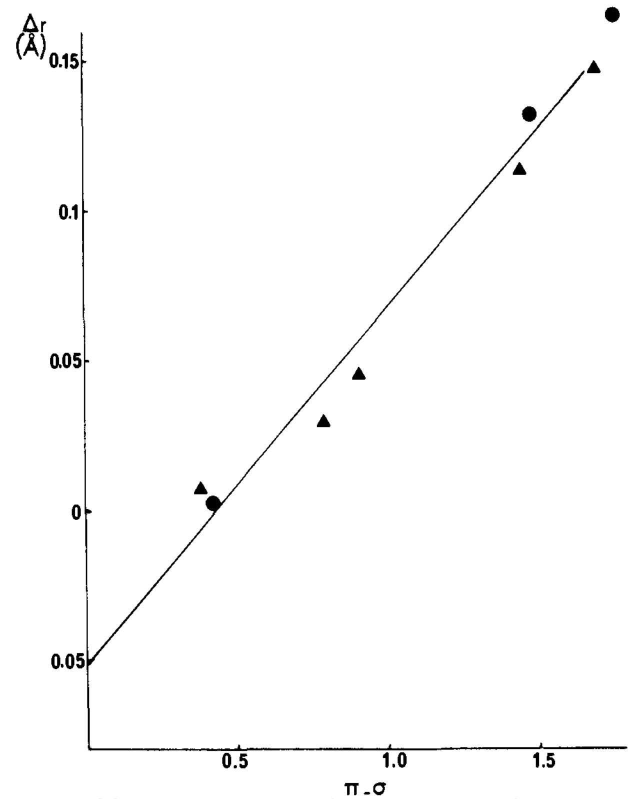

Figure 4. CO bond lengthening vs. effective charge transfer (▲, 4-31G; ●, 6-31G*).

Here the numerical coefficients are expressed in Å and Å e^{-1} for Δr in Å and ($\pi - \sigma$) in e. The constant −0.0502 Å can be interpreted in terms of an overlap repulsion due to the presence of the lithium atom(s), which is expected to be nearly constant for the range of Li–C distances used here.

The variation of the normalized change in force constant is also found to depend linearly on ($\pi - \sigma$)

$$-\frac{K_R - k_r}{k_r} \simeq 0.095 + 0.315(\pi - \sigma) \qquad (2)$$

with 0.315 in e^{-1}.

In conclusion we think that the results presented here show that the modifications of the IR spectra of C–O complexes isolated in rare gas matrices can be interpreted by quantum mechanical calculations at the SCF level. The perturbation of the frequencies and intensities by the matrix is generally small compared to the effect of the complexation itself. However, in some cases [for example, $Li(CO)_2$] the matrix perturbation is sufficient to modify the equilibrium geometry.

(VII) A Charge-Transfer Interpretation

Perhaps the simplest way to understand the results presented here, together with the experimental infrared spectra,[1] for the Li–CO species in the matrix is to picture them as charge transfer complexes between Li^+ and CO^-. Thus, for example, the 1:1 LiCO complex can be understood as a complex formed by initial total transfer of the electron from Li to CO, where it is accepted into the lowest empty orbital, the antibonding π_{CO}^* orbital. The resulting "no bond" structure between Li^+ and CO^- is stabilized by interaction with the Li–CO "charge transfer" structure.[23] The wavefunction ψ_0 for the no bond structure now has π symmetry, as does the ψ_1 wavefunction for the charge transfer structure. The electron is accepted in the latter into an extended π^* orbital pictured as

$$\pi^* = 2p_{Li} + 2p_C - 2p_O$$

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[22] Similar effects have been discussed: McIntosh, D.; Ozin, G. *J. Am. Chem. Soc.* **1976**, *98*, 3167.

[23] For example, see the discussion in the following: Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

antibonding between C and O atoms and bonding between Li and C. In addition there is some σ-bonding from the C atom lone pair toward the Li^+ ion.

In this description, the electron donor molecule is CO^-, both for the π bond and for the σ bond, while Li^+ is the electron acceptor. The Li^+CO^- complex we are describing is a pure example of an "intimate ion pair" isolated as a complex. In this description we see from the Mulliken charges described in part 3 for LiCO that 0.507 e (1 − 0.493) is transferred from CO^- to Li^+ in the π^* orbital and 0.298 e is transferred in the same direction in the σ bond. Hence the Li^+ charge is almost completely neutralized by the charge transfer but the valence electron transferred back to Li^+ has considerably more p character than s character, as it would have in an ordinary (Li, CO) no bond state (for example, in the $^2\Sigma$ electronic state of Li–CO).

According to this model, the electron transferred into the antibonding π_{CO}^* orbital in CO^- will reduce the force constant from that in CO because occupation of this extra antibonding orbital reduces the bond order from 3 in CO to 2.5 in CO^-. Hence the force constant ratio is predicted to be $K_R/k_r = 2.5/3 = 0.83$. In the charge transfer structure ψ_1, this electron is in the extended π^* antibonding orbital given above. It is still antibonding between C and O, to the same extent, so the predicted force constant ratio is still 0.83. This prediction compares very favorably with the value in Table I for the 6-31G* calculation (0.82) *and* from experiment ($K_R/k_r = 0.84$).

If the electron transferred from Li goes into the π^* orbital, and if the 2p AOs from all three atoms appear in π^* with equal coefficients as indicated above, then we might expect the p electron density on Li^+ to be 0.33 instead of 0.50, as shown above. To us, this difference does not appear to be unreasonable.

Perhaps the clearest indication of the charge transfer character of the $^2\Pi$ ground state for Li^+CO^- comes from the discussion in section III of the dependence of the calculated ratio, ω/ω_0, for the CO stretching frequencies on the Li–C distance. The $Li^+\cdots CO^-$ separated ion pair will have an energy $I_{Li} - E_{CO}$ (I is the ionization potential of Li; E is the electron affinity of CO) above the energy of separated ground state atoms, Li + CO [or about $5.39 - 0 \simeq 5.4$ eV above Li(^{2}S) + CO]. The coulomb attraction, C, and valence interaction, V, stabilize the ion pair ($C \simeq 5.0$ eV at $R_{LiC} \sim 2.0$ Å; $V \simeq 0.5$ eV), so that the $^2\Pi$ Li^+CO^- curve has an avoided crossing with the purely dissociative $^2\Pi$ Li(^{2}P) + CO($^1\Sigma$) curve (see Figure 13.1 of reference 23 for a discussion of this situation in the analogous Li^+F^- charge transfer complex). According to the results quoted above for ω/ω_0, this avoided crossing occurs for R_{LiC} between 2.1 and 2.5 Å, according to our calculation here. This interaction between the ion pair Li^+CO^- $^2\Pi$ state and the dissociative $^2\Pi$ Li(^{2}P) + CO($^2\Sigma$) state appears to be the simplest explanation both for the stability of the $^2\Pi$ state and for its "avoided crossing" character.

Once we realize the ion pair nature of the Li^+CO^- interaction, it is easy to understand the other complexes formed and their infrared spectra. In the 1:2 $Li(CO)_2$ complex, for example, the Li atom donates its electron to two CO molecules which share it equally in π_{CO}^* orbitals. The extended π^* orbital involves both π_{CO}^* orbitals and the Li 2p orbitals and is antibonding between both pairs of C and O oribtals and bonding between Li and C atoms. The antibonding contribution of the electron to the CO bond is expected to be about one-half of that in Li^+CO^-, so the force constant ratio K_R/k_r is predicted to be $2.75/3.0 = 0.92$ for $Li(CO)_2$, compared with 0.85 from the 6-31G* calculation or 0.74 from experiment. In fact, the latter values suggest that the antibonding contribution from the electron in the extended π^* orbital is the same as in the corresponding orbital for Li^+CO^-, which is probably more reasonable than to picture the CO molecules in competition for this electron.

Finally, we note that in the 2:1 Li_2CO complex, two electrons are donated to the antibonding π_{CO}^* orbital of CO^-, or to the corresponding extended π^* orbital in Li^+--CO^{2-}--Li^+. Hence, the bond order is only 2, and the value of K_R/k_r is predicted to be $2/3 = 0.67$. The two electrons are contained in the extended π^* orbital, which can hold a total of 4 electrons because of the x and y degeneracy, so the electronic states are like those for O_2, with the $^3\Sigma^-$ state expected to be lowest in energy. The predicted ratio of force constants agrees reasonably well with the value ($K_R/k_r \simeq (\omega/\omega_0)^{1/2} \simeq 0.77$) for the 6-31G* calculation.

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Registry No. LiCO, 103173-65-5; $Li(CO)_2$, 105121-67-3; Li_2CO, 105139-44-4.

Molecular Dynamics Simulations of α-D-Glucose

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Abstract: Molecular dynamics simulations were performed for α-D-glucose in vacuo in the $^1C_4$ and $^4C_1$ conformations, using the most developed semiempirical potential energy surface available for carbohydrates, as a test of the suitability of this function for representing molecular motions and to explore the dynamical fluctuations of pyranoid rings. Contrary to the assumption of rigid-ring geometry frequently employed in conformational studies of polysaccharides, the glucopyranose molecules were found to exhibit considerable flexibility and to undergo a variety of conformational fluctuations and even transitions. As in previous energy minimization studies, the $^4C_1$ conformer was found to be more stable, and the free-energy difference between the two forms was calculated to be 2.44 kcal/mol, in accord with previous estimates. The mean dynamical structure for the glucose molecule with this potential energy is acceptably close to the experimentally determined crystal structure, with the most important deviation being in the ring geometry about the C5 carbon atom and the O5 oxygen atom.

I. Introduction

In recent years the structure and dynamics of polypeptides, proteins, and nucleic acids have received considerable attention, both experimentally and theoretically.[1,2] The most abundant of biological molecules, however, the carbohydrates, have not been the focus of intensive theoretical study. A number of conformational energy studies of simple sugars and disaccharides have elucidated the main features of oligosaccharide conformational

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(1) Karplus, M.; McCammon, J. A. *Annu. Rev. Biochem.* **1983**, *53*, 263.

(2) Scheraga, H. A. *Biopolymers* **1981**, *20*, 1877.

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