

Compliant fields for molecular interactions I : Lithium cation with carbonyl donors

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Abstract. The CNDO/Force method has been employed in the determination of quadratic potential functions for the complexes of lithium cation with formaldehyde and formamide. The O, Li⁺ stretching frequency and the COLi⁺ bending frequencies have been estimated after scaling, the stretching and stretch-stretch elements of the force constant matrix. The transferability of the donor potential function to the complex has been verified.

Keywords. Ion-molecular interactions ; CNDO/Force method ; compliance constants.

1. Introduction

Alkali metal salts dissolved in non-aqueous electron-donor solvents give rise to characteristic bands of low frequency in the infrared spectrum, which have been attributed to metal ion-solvent cage vibrations (Rao 1973 ; Kecki 1973 ; Gardiner 1977 ; Irish and Brooker 1976). In the case of lithium cation, for example, this band appears around 400 cm⁻¹ and is largely dependent on the polarity of the solvent as well as the nature of the anion. In order to gain some insight into the nature of ion-molecule interactions, a simple 1 : 1 model containing one solvent molecule associated with one ion finds considerable application. This two body potential is expected to dominate in much more complicated situations existing in the actual liquid state (Schuster *et al* 1975a). The 'supermolecule' approach (Pullman and Pullman 1975) in which an ion and its attendant solvent molecule (or molecules) are treated as a single molecular entity, facilitates the use of quantum chemical molecular orbital methods in investigating ion-molecule interactions theoretically. Rao (1976) has extensively reviewed the work done in the study of metal-ligand interactions.

Wong *et al* (1971) have studied the interaction of alkali metal ions with acetone and have reported ion-oxygen stretching vibrational frequencies : for the interaction of Li⁺ with acetone this frequency occurs around 425 cm⁻¹. The influence

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of electrolytes on the fundamental frequencies of acetone have also been reported by several workers (Pullin and Pollock 1958; Yamada 1960; Gulik-Krzywicki and Kecki 1965; Perelygin 1969; Gadzhiev and Pominov 1965; Driessen and Groeneveld 1969). The C=O stretching frequency has either been split or shifted to lower frequencies in these studies. The influence of electrolytes on the vibrational spectrum of formamide has been the subject of several investigations (Perelygin *et al* 1968; Gardiner *et al* 1975; Bukowska 1978; Rao *et al* 1972; 1973, 1979; Lees *et al* 1979). In the study by Lees *et al* (1979), the Li⁺—O stretching vibration has been observed at about 370 cm⁻¹ for LiCl : 2.5 HCONH₂. Absorption in the range 355–370 cm⁻¹ has been reported by Lees and coworkers (1979) for lithium salts in general.

In contrast to several experimental reports on metal-solvent cage vibrations in the range 200–500 cm⁻¹, very few theoretical calculations to predict these vibrations have been attempted, even at the *ab initio* level. Most theoretical studies of ion-molecule interactions have been confined to the energetics of interaction and these studies have been reviewed by Schuster and coworkers (1975a). The Li⁺—O stretching force constant in lithium-formaldehyde complex, used as a model for studying the Li⁺—acetone system, has been calculated by Gupta and Rao (1973). The *ab initio* calculations of Sadlej (1980) on the Li⁺—H₂CO₂ system show that the C=O stretching force constant is larger than that in H₂CO which although in accordance with the CNDO/2 calculations of Sadlej and Kecki (1971) on the interaction of acetone with a cation, is contrary to what one would expect following interaction involving electron donation. In the case of the Li⁺—formamide complex, the metal-oxygen stretching force constant has been estimated by the CNDO/2 energy method by Gupta and Rao (1973). Recently, Bukowska and Miaskiewicz (1981) have investigated the vibrational frequency shifts of three characteristic stretching modes of formamide (CO, NH and CN) and have estimated the force constants for the complex formed, by CNDO/2 energy method. However, no attempt has been made to estimate or experimentally determine the Li⁺—O stretching frequency. In several of the studies cited above complete optimization of the geometry of the 'supermolecule' has not been effected and optimization of the O—Li⁺ distance alone has been carried out, the rest of the molecule being constrained to the experimental geometry.

In recent years, quantum chemical methods have been increasingly used to calculate potential functions of molecules (Pulay 1976; Duncan 1975). Pulay and Torok (1973, 1978) have applied the force method (Pulay 1969) to CNDO/2 wave functions and have calculated equilibrium geometries as well as quadratic force constants. Annamalai *et al* (1976, 1978, 1982) have also employed the CNDO/Force (CNDO/F) method to several molecules of interest. It has been observed in these studies that the stretching force constants (diagonal and off-diagonal) are overestimated by the CNDO/F method while other force constants are determined reasonably well. The MNDO-MOCIC method developed by Swanson *et al* (1978) is based on the compliance constant formalism advocated by Taylor and Pitzer (1947); Maslou (1949); Decius (1963) and Jones and Ryan (1970). Compliance constants being uniquely defined and independent of the definition of the basis coordinates, are expected to be transferable between chemically similar molecules. Compliance constants for a few molecules have been calculated by Murthy and Ranganathan (1982a–e), using the CNDO/F method.

In view of the lack of meaningful data regarding ion-molecule interactions, it was considered interesting to optimize the geometries of 1:1 complexes of lithium cation with formaldehyde and formamide as well as to determine the force constants for these complexes by CNDO/F method. Redundancy-free internal compliance constants for the donor systems have already been calculated by Murthy and Ranganathan (1982d and e).

2. Theoretical approach

The force constants F_{ij} , defined as

$$F_{ij} = (\partial^2 E / \partial R_i \partial R_j),$$

where E is the total energy of the molecule and R_i, R_j are their internal coordinates, are evaluated by analytical differentiation of the energy followed by numerical differentiation of the forces obtained in the first step, with respect to the internal coordinates (Pulay 1969). Among the various semiempirical MO methods available, Torok and Pulay (1978) found the CNDO/2 and INDO methods to yield better results than MINDO/2. The CNDO/F calculations in the present study were carried out using a modified version (Kanakavel *et al* 1976) of the CNDO/2 computer program (Pople and Beveridge 1970), incorporating Pulay's procedure (1969). Starting with a trial geometry, the force acting on each atom is calculated and by allowing the atoms to relax in the direction of the forces, f_i , the equilibrium geometry is arrived at. The molecule at the equilibrium geometry is subjected to distortions describing the vibrations of the molecule, and the forces computed in each case. The deformations $\pm \Delta R_i$ in the i th internal coordinate are of the order of $\pm 0.01\text{\AA}$ for stretching modes and $\pm 1^\circ$ for bending modes. The internal forces are obtained by suitable transformation of the cartesian forces computed by the program (Kanakavel *et al* 1976). The force constants F_{ij} are evaluated from the internal forces f by numerical differentiation:

$$F_{ij} = -\Delta f_i / \Delta R_j; \quad F_{ji} = -\Delta f_j / \Delta R_i, \\ F_{ij} \approx F_{ji}.$$

The vibrational secular equation in terms of compliance constants is

$$[CK - \Phi E] = 0,$$

where C is the compliance constant matrix, K the kinetic energy matrix and Φ is a diagonal eigenvalue matrix of elements $\phi_i = (4\pi^2 c^2 v_i^2)^{-1}$. The compliance constant matrix is the inverse of the force constant matrix F and characterizes the molecule just as completely as the F matrix.

One of the important advantages of the use of compliants is that the C matrix is invariant to the choice of coordinates. Therefore, when redundancy conditions exist among the internal coordinates, the compliants involving the redundancy are uniquely defined as zero. This is not true of the force constants involving a redundancy, which become indeterminate. Also, as the compliants C_{ij} are dependent on the coordinates i or j alone and independent of other coordinates, transferability of compliance constants among related molecules becomes justifiable.

The initial C matrix is computed as the inverse of the force constant matrix. The G matrix (which is the inverse of the K matrix) elements are obtained by the method of Schachtschneider (1964) and the frequencies are calculated from the C and G matrices with the help of program COMPLY (Swanson and Ottlinger). All the calculations were carried out on an ICL 2960 computer.

3. Results and discussion

The approximations involved in the semiempirical CNDO/2 method lead to unrealistic geometries for metal ion—electron donor complexes. Rao (1973)

Table 1. CNDO/F geometries* and interaction energies* of complexes of lithium cation with formaldehyde and formamide.

Bond parameter	Complex	Donor	Complex (Ref)†
Li⁺—H₂CO :			
r_{CO}	1.256	1.241	1.21°
r_{OLi^+}	2.288	...	1.84
r_{CH}	1.113	1.114	1.12°
$\angle HCH$	118.4	116.3	118.0°
$\angle COLi^+$	180.0	...	180.0
E_{INT}	31.2	...	44.2
Li⁺ — HCONH₂ :			
r_{CO}	1.284	1.263	1.212°
r_{OLi^+}	2.248	...	1.71
r_{CH}	1.112	1.116	1.125
r_{CN}	1.343	1.358	1.368°
$r_{NH(cis)}$	1.064	1.060	1.027°
$r_{NH(trans)}$	1.062	1.057	1.027°
$\angle OCN$	123.1	123.8	125.0°
$\angle HCN$	117.4	115.3	112.7°
$\angle HNH$	115.0	115.2	...
$\angle CNH (cis)$	121.9	121.1	118.7°
$\angle CNH(trans)$	123.1	123.7	119.7°
$\angle COLi^+$	180.0°	...	180.0
E_{INT}	39.4	...	55.9

Cis and trans with respect to C = O bond

* Distances in Å, Angles in degrees and Energies in kcal mole⁻¹

† Reference for formaldehyde complex : Schuster *et al* (1975b)
and for formamide complex : Rude *et al* (1974)

° Constrained values

has arrived at an LiOC angle of 60° for complexes of Li^+ with H_2CO and HCONH_2 , the complex being planar in the case of formaldehyde donor and the lithium ion placed perpendicular to the molecular plane in the case of formamide donor. Such strange geometries have been proved to be an artefact of the CNDO method (Schuster *et al* 1975a; Rode 1974). In contrast, *ab initio* calculations have invariably resulted in a linear COLi^+ arrangement (Schuster *et al* 1975a). Recent thorough x-ray crystallographic investigations (Chakrabarti *et al* 1981) on N-methylacetamide complexes of Li, Na, K, Mg and Ca have shown that metal ions deviate from the direction of the lone pair of the carbonyl oxygen. Deviation from the lone pair direction is generally found in other oxygen donor complexes of alkali and alkaline earth metal cations (Poonia and Bajaj 1979). In the present study however, the geometry optimization was restricted to a linear COLi^+ arrangement. The CNDO/F optimized geometries of the complexes of lithium cation with formaldehyde and formamide are compared with the CNDO/F optimized geometries of the donor systems (Murthy and Ranganathan 1982d and e) in table 1. The O—Li⁺ distances and the interaction energies of the complexes have been compared with *ab initio* results (Schuster *et al* 1975b; Rode and Preuss 1974). The geometry of the Li^+ — HCONH_2 complex has also been calculated by Corongiu *et al* (1980) using *ab initio* wavefunctions and is not very different from that reported by Rode and Preuss (1974). The changes observed in the C=O and C—N bond lengths are consistent with chemical facts. The greater energy of interaction for the formamide complex over the formaldehyde complex is in agreement with the *ab initio* results of Del Bene (1979). The CNDO/F optimized geometries have been used to calculate the *G* matrix elements, based on the redundancy-free internal coordinates listed in table 2. Figure 1 illustrates the internal coordinates of the complexes under investigation.

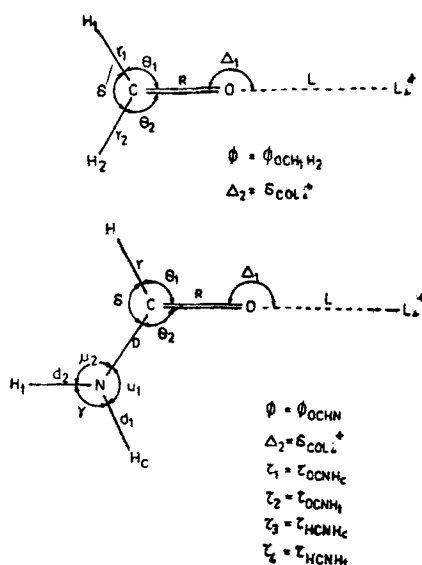


Figure 1. Internal coordinates of lithium cation complexes with formaldehyde and formamide.

Table 2. Redundancy-free internal coordinates for lithium cation complexes with formaldehyde and formamide.

Coordinate	Description
Li⁺—H₂CO :	
In-plane :	
1. $R_1 = \Delta R$	CO stretch
2. $R_2 = \Delta L$	OLi ⁺ stretch
3. $R_3 = \Delta r_1$	CH stretch
4. $R_4 = \Delta r_2$	CH stretch
5. $R_5 = 6^{1/2} (2\Delta\delta - \Delta\theta_1 - \Delta\theta_2)$	HCH deform
6. $R_6 = 2^{-1/2} (\Delta\theta_1 - \Delta\theta_2)$	CO rock
7. $R_7 = \Delta (\Delta_1)$	COLi ⁺ bend
Out-of-plane :	
1. $R_8 = \Delta\phi$	CO wag
2. $R_9 = \Delta (\Delta_2)$	COLi ⁺ bend
Li⁺—HCONH₂ :	
In-plane :	
1. $R_1 = \Delta R$	CO stretch
2. $R_2 = \Delta L$	OLi ⁺ stretch
3. $R_3 = \Delta r$	CH stretch
4. $R_4 = \Delta D$	CN stretch
5. $R_5 = 2^{-1/2} (\Delta d_1 + \Delta d_2)$	NH ₂ stretch
6. $R_6 = 2^{-1/2} (\Delta d_1 - \Delta d_2)$	NH ₂ stretch
7. $R_7 = 6^{-1/2} (2\Delta\delta - \Delta\theta_1 - \Delta\theta_2)$	NCH deform
8. $R_8 = 2^{-1/2} (\Delta\theta_1 - \Delta\theta_2)$	CO rock
9. $R_9 = 6^{-1/2} (2\Delta\gamma - \Delta\mu_1 - \Delta\mu_2)$	NH ₂ deform
10. $R_{10} = 2^{-1/2} (\Delta\mu_1 - \Delta\mu_2)$	NH ₂ wag
11. $R_{11} = \Delta (\Delta_6)$	COLi ⁺ bend
Out-of-plane :	
1. $R_{12} = \Delta\phi$	CO wag
2. $R_{13} = \Delta (\Delta_2)$	COLi ⁺ bend
3. $R_{14} = 2^{-1} (\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4)$	NH ₂ torsion
4. $R_{15} = 2^{-1} (\Delta\tau_1 - \Delta\tau_2 + \Delta\tau_3 - \Delta\tau_4)$	NH ₂ wag

The CNDO/F force constants evaluated for the Li⁺—H₂CO and Li⁺—HCONH₂ systems are presented in tables 3 and 4 respectively. It is noticed that the CNDO/F estimates of the diagonal stretching force constants of Li⁺—H₂CO (cf. table 3) differ considerably from those of H₂CO (Murthy and Ranganathan 1982d). For example, the C = O stretching force constant has been calculated to be 32.687 mdynA⁻¹ for Li⁺—H₂CO and 34.214 mdyn A⁻¹ for H₂CO. This is expected,

Table 3. Redundancy-free internal compliance constants for lithium cation formaldehyde complex.

Force constant†	Calc. (*) CNDO/F	Calc. for H ₂ CO	Final values	Compliance constant†	Calc. (*)
F _{1,1}	32·687	12·881	12·305	C _{1,1}	0·087
F _{1,2}	— 0·905	...	— 0·453	C _{1,2}	0·066
F _{1,3}	0·539	0·469	0·469	C _{1,3}	— 0·009
F _{1,5}	— 0·504	— 0·427	— 0·427	C _{1,5}	0·067
F _{2,2}	1·170	...	0·585	C _{2,2}	1·761
F _{2,3}	0·027	...	0·014	C _{2,3}	— 0·012
F _{2,5}	0·024	...	0·024	C _{2,5}	0·023
F _{3,3}	11·854	4·334	4·369	C _{3,3}	0·234
F _{3,4}	0·142	0·142	0·142	C _{3,4}	— 0·009
F _{3,5}	0·636	0·020	0·020	C _{3,5}	— 0·016
F _{3,6}	— 0·107	— 0·142	— 0·142	C _{3,6}	0·040
F _{3,7}	— 0·047	...	— 0·047	C _{3,7}	0·114
F _{5,5}	0·631	0·541	0·541	C _{5,5}	1·902
F _{6,6}	0·841	0·856	0·856	C _{6,6}	1·181
F _{6,7}	0·005	...	0·005	C _{6,7}	— 0·025
F _{7,7}	0·098	...	0·098	C _{7,7}	10·327
F _{8,8}	0·491	0·399	0·399	C _{8,8}	2·567
F _{8,9}	0·043	...	0·043	C _{8,9}	— 0·563
F _{9,9}	0·197	...	0·197	C _{9,9}	5·197

* This work

†Units for force constants: stretch-stretch in m dyn A⁻¹; stretch-bend in m dyn rad⁻¹; Bend-Bend in m dyn a rad⁻²; and Compliance constants: stretch-stretch in a m dyn⁻¹; stretch-bend in rad m dyn⁻¹; Bend-Bend in rad² A⁻¹ m dyn⁻¹.

from the change in the C = O bond length (cf. table 1). Sadlej (1980), however has calculated these force constants to be 14.50 m dyn A⁻¹ for H₂CO and 16.15 m dyn A⁻¹ for the Li⁺ complex. An initial calculation after scaling the stretching force constants and the stretch-stretch interaction constants by 0.5 (Murthy and Ranganathan 1982 a and b), yielded good estimates of the Li⁺-O stretching frequency (around 400 cm⁻¹) which is in good agreement with the experimental value for the lithium ion—acetone system (Wong *et al* 1971). However, other frequencies were not reliable enough for determining frequency shifts of the donor molecule upon complexation. This is because the CNDO/F force constants require considerable refinement with experimental frequencies before the frequency shifts can be evaluated. Unfortunately, experimental frequency data is not available for 1:1 metal-ligand complexes. Under the circumstances, a viable solution was to transfer the refined potential function of the donor to that of the complex. The scaled force constants for the three new coordinates of the complex,

Table 4. Redundancy-free internal compliance constants for lithium cation-formamide complex.

Force constant†	Calc. (*) CNDO/F	Calc. for HCONH ₂	Final values	Compliance constants†	Calc (*)
F _{1,1}	30.380	12.301	12.121	C _{1,1}	0.091
F _{1,2}	0.406	...	0.203	C _{1,2}	— 0.026
F _{1,3}	0.598	0.478	0.478	C _{1,3}	— 0.006
F _{1,4}	2.631	2.109	2.109	C _{1,4}	— 0.026
F _{1,7}	— 0.081	— 0.604	— 0.604	C _{1,7}	0.069
F _{1,8}	— 0.484	— 0.074	— 0.074	C _{1,8}	— 0.024
F _{1,11}	— 0.029	...	— 0.029	C _{1,11}	0.059
F _{2,2}	1.248	...	0.642	C _{2,2}	1.582
F _{2,4}	0.188	...	0.094	C _{2,4}	— 0.011
F _{2,7}	0.014	...	0.014	C _{2,7}	— 0.059
F _{2,8}	— 0.023	...	— 0.023	C _{2,8}	0.064
F _{2,11}	— 0.014	...	— 0.014	C _{2,11}	0.499
F _{3,3}	11.662	4.575	4.591	C _{3,3}	0.220
F _{3,4}	0.465	0.441	0.441	C _{3,4}	— 0.012
F _{3,7}	0.102	0.010	0.010	C _{3,7}	0.001
F _{3,8}	0.213	0.071	0.071	C _{3,8}	— 0.027
F _{3,10}	0.072	0.026	0.026	C _{3,10}	— 0.007
F _{4,4}	20.076	7.680	7.766	C _{4,4}	0.143
F _{4,5}	0.531	0.456	0.456	C _{4,5}	— 0.010
F _{4,6}	0.038	0.036	0.036	C _{4,6}	— 0.001
F _{4,8}	— 0.589	— 0.308	— 0.308	C _{4,8}	0.071
F _{4,9}	— 0.320	— 0.278	— 0.278	C _{4,9}	0.087
F _{4,10}	— 0.077	— 0.069	— 0.069	C _{4,10}	0.008
F _{4,11}	0.014	...	0.014	C _{4,11}	— 0.065
F _{5,5}	14.963	6.738	6.725	C _{5,5}	0.149
F _{5,9}	0.167	0.004	0.004	C _{5,9}	— 0.007
F _{6,6}	14.260	6.676	6.635	C _{6,6}	0.151
F _{6,7}	0.075	0.010	0.010	C _{6,7}	— 0.001
F _{6,8}	0.042	0.008	0.008	C _{6,8}	— 0.002
F _{6,10}	0.196	0.020	0.020	C _{6,10}	0.006
F _{7,7}	0.826	0.882	0.882	C _{7,7}	1.299
F _{7,8}	0.153	0.235	0.235	C _{7,8}	— 0.437
F _{7,9}	— 0.019	— 0.010	— 0.010	C _{7,9}	0.007
F _{7,10}	0.068	0.037	0.037	C _{7,10}	— 0.011
F _{8,8}	0.884	0.712	0.712	C _{8,8}	1.618
F _{8,10}	0.023	0.103	0.103	C _{8,10}	— 0.259
F _{9,9}	0.532	0.454	0.454	C _{9,9}	2.258
F _{10,10}	0.544	0.558	0.558	C _{10,10}	1.840
F _{11,11}	0.044	...	0.044	C _{11,11}	23.052
F _{12,12}	0.618	0.549	0.549	C _{12,12}	1.822
F _{13,13}	0.054	...	0.054	C _{13,13}	18.692
F _{14,14}	0.038	0.015	0.015	C _{14,14}	65.041
F _{15,15}	0.077	0.066	0.066	C _{15,15}	15.136

* This work † Units as in table 3

Table 5. Calculated frequencies (in cm^{-1}) for lithium cation formaldehyde complex.

Species	H_2CO^*	$\text{Li}^+-\text{H}_2\text{CO}$	Approximate Description
A_1	2796.9	2802.4	CH stretch
	1750.4	1738.2	CO stretch
	1510.5	1514.4	HCH deform
	...	402.0	OLi^+ stretch
B_2	2855.7	2858.0	CH stretch
	1257.7	1260.4	CO rock
	...	169.0	COLi^+ bend
B_1	1168.2	1179.4	CO wag
	...	245.1	COLi^+ bend

* H_2CO gas phase frequencies from Murthy and Ranganathan (1982d)

Table 6. Calculated frequencies (in cm^{-1}) for lithium cation-formamide complex

Species	HCONH_2^*	$\text{Li}^+-\text{HCONH}_2$	Approximate Description
A'	3533	3514	NH_2 stretch
	3413	3427	NH_2 stretch
	2880	2883	CH stretch
	1713	1686	CO stretch
	1594	1535	NH_2 deform
	1402	1422	HCN deform
	1286	1301	CN stretch
	1091	1076	NH_2 rock
	563	552	CO rock
	...	421	OLi^+ stretch
A''	...	88	COLi^+ bend
	1046	1091	CO wag
	602	592	NH_2 wag
	289	282	NH_2 torsion
...	119	COLi^+ bend	

* HCONH_2 solution phase frequencies from Murthy and Ranganathan (1982e)

viz. $\text{O}-\text{Li}^+$ stretching and in-plane and out-of-plane COLi^+ bending modes as evaluated by the CNDO/F method were introduced into the refined force constant matrix (obtained by the inversion of the refined compliance constant matrix of the donor). Since there is significant variation in the diagonal stretching force constants of the donor molecule upon complexation, it was necessary to normalize these diagonal elements by a factor of magnitude F (complex)/ F (donor). For

example, the factor is 32.687/34.214 for the C = O stretching mode in Li⁺—H₂CO complex. The resulting force constants are shown in column 4 of table 3.

A similar approach has been adopted in the case of Li⁺—HCONH₂. These force constants have been used to construct the compliance constant matrices, which in turn, have been used to calculate the frequencies of vibration for the complexes of Li⁺ with H₂CO and HCONH₂. These frequencies have been compared with the fundamentals of the donor systems (as calculated by Murthy and Ranganathan 1982d and e) in tables 5 and 6 respectively. Approximate descriptions of the vibrational frequencies of the complexes are also given in these tables, based on their potential energy distributions. Any comparison of the frequencies calculated in this study with those of Bukowska and Miaskiewicz (1981) is not valid because of the differences in experimental conditions.

In the Li⁺—H₂CO complex, the C = O stretching frequency shifts to a value lower by 12 cm⁻¹. The observed C = O shift for the Li⁺ complex with acetone is only about -4 cm⁻¹ (Gulik-Krzywicki and Kecki 1965). It is interesting that the asymmetric and symmetric C—H stretching frequencies shift to higher values on complexation. The O—Li⁺ stretching frequency is calculated to be 402 cm⁻¹, and this value is in excellent agreement with the range of experimental frequencies obtained with several donors (Rao 1973). The calculated COLi⁺ linear bending modes at 169 cm⁻¹ (in-plane) and 245 cm⁻¹ (out-of-plane) have still not been experimentally identified.

For the formamide complex, the C = O stretching frequency shift is more pronounced and calculated to be -27 cm⁻¹. The N—H, C—H and C—N stretching modes are all shifted to higher frequencies. The predicted shift of the C—H stretching vibration to higher frequencies is in agreement with the experimental observation of Bukowska and Miaskiewicz (1981). The O—Li⁺ stretching frequency has a value of 421 cm⁻¹ which is in agreement with the value predicted by Rao (1973). The COLi⁺ linear bending modes are estimated to occur at 88 cm⁻¹ (in-plane) and 119 cm⁻¹ (out-of-plane).

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