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Modeling structure and spectra of silver complexes in condensate films of polar liquid crystals

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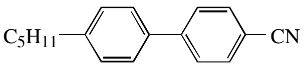
By performing *ab initio* quantum chemistry calculations, including partial geometry optimization and vibrational analysis for the sandwich-like cyanobenzene–silver complexes, it is shown that the observed red shifts in the CN stretching region of the IR spectra of silver–cyanobiphenyl condensate films should be assigned to the formation of the -complexes.

The materials formed by co-condensation of metal atoms and organic mesogen molecules exhibit interesting properties which promise important technological applications.[1] The reactions of metals with the molecules composing liquid crystals, in particular, cyanobiphenyl derivatives, are carried out under low-temperature conditions by condensing the molecular beams into thin films, and IR and UV spectral techniques are used to characterize the reaction products.[2,3] However, little is known about the structure of these intriguing substances and the experimental spectral patterns deserve theoretically motivated interpretations.

The studies of silver complexes with the 4-pentyl-4′-cyanobiphenyl (5CB) molecules described in refs. 2 and 3 showed that (1), the strong IR band at 2230 cm^{-1} assigned to the CN stretching vibration characterised the spectrum of the pure 5CB film and (2), two new bands at 2080 and 2030 cm^{-1} appeared in the samples obtained upon co-condensation of 5CB with silver.



5CB

The tentative assignment of these spectral features was carried out following the trends in chemistry of the transition metal complexes with unsaturated organic molecules.[4] The vibrational spectral shifts due to such complexation may amount by up to several hundred wavenumbers,[5] therefore, the red shifts of 150 and 200 cm^{-1} in the silver–5CB condensates compared to the pure 5CB have been qualitatively explained by the formation of -type complexes.[3]

The aim of this work is to perform a theoretical analysis of the complexes which can be formed in condensate films and to suggest a model consistent with the observed IR spectral shifts. Presently, the modern methods of *ab initio* quantum chemistry can be applied for fairly extended molecular systems, however, the standard approaches of quantum chemistry molecular modeling, namely, a search of the global minimum on the potential energy surface with subsequent vibrational analysis have limited value in this case, since we intend to simulate properties of the bulk, but not of the gas phase system. Moreover, the only vibrational degrees of freedom indicative in the spectrum, namely, the vibrations of the CN groups of the ligands, are directly probed in the experiments, and the modeling should be oriented on these particular features.

Therefore, we apply here the following strategy. The complete *ab initio* geometry optimization and vibrational analysis based on quantum chemistry calculations is performed for the 5CB molecule and for its most important fragment, cyanobenzene PhCN. The reference value of the strong IR band assigned to the CN vibrations is deduced by comparison to that in the silver complexes. A series of calculations was then carried out for the sandwich-like complex $Ag(PhCN)_2$ with the majority of geometry parameters fixed. An analysis of the electron density distributions as well as the curvatures of the potential energy surfaces along the C–N coordinates allows us to estimate the spectral shifts for the CN vibrations and to formulate a structural model consistent with the observed spectral patterns of the Ag/5CB films.

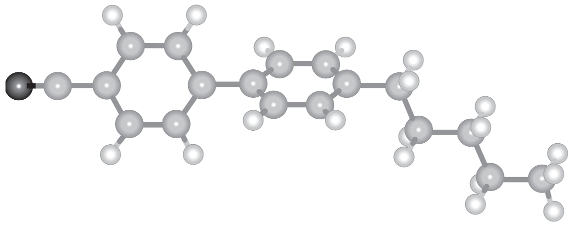


Figure 1 The stucture of the 5CB molecule corresponding to the minimum on the potential energy surface.

We have used the GAMESS quantum chemistry package[6] operational on an Intel-based Pentium Pro workstation. The conventional Stevens–Basch–Krauss (SBK) pseudopotentials on all heavy atoms with the corresponding basis sets[7] were employed.

Figure 1 shows the stucture of the 5CB molecule referring to the minimum of the potential surface in the Hartree–Fock approximation. This structure is very close to that predicted by the density functional calculations,[8,9] and even such a delicate parameter as the torsional angle between the benzene rings (44°) is nicely reproduced by our calculations. The frequency of the normal vibration easily recognized as the CN stretch equals 2497 cm^{-1}. The same treatment of the cyanobenzene molecule PhCN gives for this vibration the frequency 2501 cm^{-1}. If the usual scaling procedure to improve the Hartree–Fock harmonic frequencies is employed with a scaling factor of 0.9, then the vibrational band predicted for both 5CB and PhCN molecules at about 2250 cm^{-1} is in excellent agreement with the observed value of 2230 cm^{-1}. An additional check of the approach is provided by a series of calculations for the PhCN molecule with different basis sets [DZV, TZV, 6-311G, 6-311G*(1d1p)] which give consistent values of the CN vibrational frequency ranging from 2500 to 2585 cm^{-1} (*cf.* 2501 cm^{-1} with the SBK option).

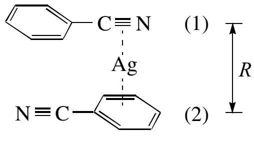
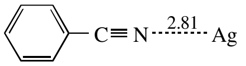
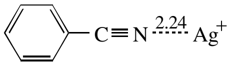


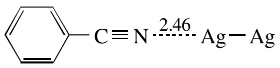
Figure 2 Model for the silver–cyanobenzene complex.

Complete geometry optimization and vibrational analysis of the free, *i.e.* not embedded into the liquid crystal matrix, species (PhCN)Ag, $(PhCN)Ag^+$ and $(PhCN)Ag_2$ lead to the conclusion that the global minima correspond to the -type complexes with the linear arrangements C–N···Ag with the N···Ag distances (in Å) shown in the picture, and the C–N vibrational frequencies shifted from the reference value for PhCN by +9, –7 and +20 cm^{-1}, respectively. Therefore, such configurations cannot be expected in the Ag/5CB films, since experimentally shifts of –150 and –200 cm^{-1} have been observed.

The structures corresponding to the -complexes were considered next. According to the X-ray investigations[10–12] the cyanobiphenyl molecules in the films are arranged in pairs







by the 'head-to-tail' principle. Therefore, we have considered a model for the silver–cyanobenzene complex shown in Figure 2.

The system possesses planar symmetry with the silver atom placed at equal distances from the ligands, namely, from the centre of the CN fragment of ligand (1) and from the centre of the ring of ligand (2). In calculations, almost all the geometry parameters were fixed at the values of the free PhCN molecule, and the distance *R* between the planar ligands (1) and (2) was varied. Partial geometry optimization was performed with the use of the Hilderbrandt type internal coordinates.

Pilot calculations showed that two Hartree–Fock solutions could compete for the ground state, one corresponding to $(PhCN)_2Ag$ and another to the charge-transfer $(PhCN)_2^-Ag^+$ configurations. Therefore, the multiconfigurational self-consistent field (MCSCF) method was used in order to take into account such a pronounced effect of electron distributions in the complex. In calculations, the orbitals were obtained by using the state averaging technique over both contributing electronic configurations. The computed dependence of total energy on the interligand distance *R* is shown in Figure 3.

This graph, together with the view of the charges on atoms computed according to the natural population analysis,[13] clearly illustrate the changes in the structure of the complex when the distance between the matrix molecules is varied. At large *R* ($R > 4.7$ Å), the neutral silver atom is embedded into the cavity between the ligands. In the vicinity of $R = 4.7$ Å a sharp change in shape of the energy curve (Figure 3) indicates a drastic modification in the electron density distribution: an electron from the silver atom jumps to the ligands, and the charge-transfer $(PhCN)_2^-Ag^+$ configuration dominates at $R < 4.7$ Å. This observation is confirmed by direct calculations of the natural electronic charges[13] on the fragments of the complex: Ag, PhCN (1) and PhCN (2).

It is important to notice that almost all electron density borrowed from silver flows into the * system of the benzene ring of the (lower in Figure 2) ligand PhCN (2), while only a small fraction of the electron charge is donated to the * orbitals of CN of the (upper in Figure 2) ligand PhCN (1).

Qualitatively, the red shifts in vibrational frequencies of the CN groups in the cyanobiphenyl–silver complexes are understood. Upon formation of the films, the silver atoms enter the cavities between the pairs of organic ligands in such a manner that asymmetric arrangements with respect to the CN groups are accomplished (a simplified picture is presented in Figure 2). Within the solid phase, the occurrence of distances between the ligands close enough to account for the charge-transfer complexes (in our simplified model for $R \leq 4.7$ Å) is justified, in particular, by the X-ray investigations.[8,9] Donation of the smaller fraction of electron density of silver to the antibonding orbitals of CN of one ligand results in an increase in the corresponding internuclear C–N distance and a decrease in the curvature of the potential surface along this coordinate, *i.e.* a decrease in the vibrational frequency. Donation of the larger fraction of the charge on Ag to the * system of another ligand leads to a redistribution of the electron density in the thus formed negative ion, with a decrease in the corresponding CN frequency by another value. In particular, in our calculations the CN vibrational frequency of pure anion $PhCN^-$ is shifted to the red compared to the neutral molecule PhCN by 220 cm^{-1}.

Table 1 Computed harmonic frequencies of the CN vibrations in the complex $(PhCN)_2Ag$ depending on the interligand distance *R* and the corresponding frequency shifts with respect to the value 2501 cm^{-1} in the free molecule PhCN.

R/Å	Frequencies and shifts/cm^{-1}			
	ω in PhCN (1)	ω	ω in PhCN (2)	ω
4.4	2351	–150	2326	–175
4.7	2392	–109	2412	–89
4.8	2416	–85	2471	–30

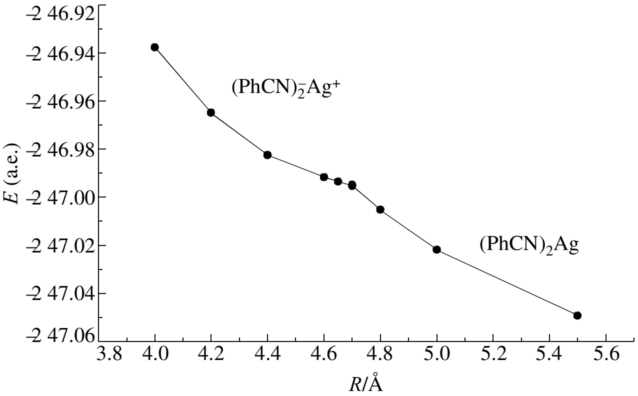


Figure 3 Energy dependence of $(PhCN)_2Ag$ on the interligand distance *R*.

We attempted to reproduce the vibrational matrix shifts at the quantitative level. For this goal again the model pictured in Figure 2 was employed. We selected 3 representative values of the interligand distances *R*, namely, $R = 4.4$ Å (charge-transfer configuration), $R = 4.8$ Å (neutral configuration) and $R = 4.7$ Å (critical point for the electron jump) and analysed the cuts through the potential energy surfaces corresponding to the C–N coordinates. First, partial non-gradient geometry optimization was performed with respect to the C–N and C–C (between the closest carbon atoms of the cyano groups and of the benzene ring) distances while keeping all other parameters fixed. Then the points on the potential surfaces around the found equilibrium C–N coordinates were computed and numerical estimates of the energy curvatures and the vibrational frequencies of the CN groups were obtained. Table 1 shows the results of these simulations.

Clearly, the conclusions of the qualitative picture described above is confirmed by the numerical data. In the case of the charge-transfer complex ($R = 4.4$ Å) the simulated red shifts in the CN vibrations (–150 and –175 cm^{-1}) correlate well with those observed experimentally for the Ag/5CB films (–150 and –200 cm^{-1}). Of course, it is difficult to expect complete agreement between values computed for the model system and those measured for the real system, however, their correspondence is good enough to confirm our understanding of the phenomena.

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