

FTIR spectroscopy and interaction potentials of some small molecules adsorbed on C₆₀

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The paper reviews our recent work on FTIR spectroscopy of some small molecules adsorbed on C₆₀. Spectra of adsorbed CO, NO, CO₂, N₂O and CH₃OH are shown and discussed. The system CO/C₆₀ is addressed in more detail. In addition to the experimental results, calculations of adsorption potentials and spectral shifts are presented.

1. INTRODUCTION

Intense interest in fullerenes had begun in 1985 with the discovery that 60-atom clusters were present in the mass spectra of laser-vaporized graphite. The experiment was done by Richard Smalley's group of Rice Institute, in collaboration with Kroto at the University of Sussex[1]. In 1990, Krätschmer and his colleagues[2] succeeded in isolating macroscopic amounts of soluble fullerene mixtures by solvent extraction of a sooty deposit produced by arc vaporization of graphite in a helium atmosphere. These mixtures were composed mostly of C₆₀ but also contained significant amounts of C₇₀ and traces of other fullerenes.

Since the preparation of fullerenes in macroscopic quantities, a huge number of publications appeared on their physical and chemical properties including a number of monographies of which the most extensive is by M.S. Dresselhaus, G. Dresselhaus and P. C. Eklund [3].

In contrast to infinite structures of diamond and graphite, the fullerenes represent a pure molecular form of the element. They are closed hollow cages comprising exactly 12 pentagons and any number of hexagons in which every carbon atom is sp² hybridized.

The 60 carbon atoms in C₆₀ are chemically equivalent. The structure contains two distinct bond types: short double bonds, 1.39 Å, and single bonds,

1.44 Å. In very pure C_{60} the spherical molecules pack in a face-centered cubic (fcc) structure. This structure contains large interstitial cavities which account for nearly 27% of the unit cell volume and results in C_{60} being less than half as dense (1.65 g/cm^3) as diamond (3.51 g/cm^3). In the solid, intermolecular bonding is analogous to the weak interplanar bonding between graphite layers and is also due to van der Waals attraction. The distance between adjacent carbon cages in solid C_{60} is 2.9 Å as compared with the 3.35 Å gap between atomic planes in graphite. The electronic structure of C_{60} results in being a good electron acceptor and a weak oxidant, causing interesting physical and photophysical properties. Some of the group 1 and group 2 metal salts of C_{60} (in which the metal ions occupy the interstices) display superconductivity at low temperature (e.g., $\text{RbCs}_2\text{C}_{60}$, $T_c=33 \text{ K}$).

The C_{60} molecule is best described as a partly delocalized electron-deficient polyalkene rather than a superaromatic molecule. Much of the reported chemistry is consistent with this description.

Despite the voluminous literature devoted to C_{60} and some other fullerenes adsorption studies on these materials are very scarce. The present short review is concerned with IR spectra of some small molecules adsorbed on high surface area C_{60} films, recorded mainly in our laboratory. The analysis of the experimental results is concerned with adsorption potential and spectral shift calculations. These were performed for adsorbed CO which acted as a model molecule (like in many other spectroscopic investigations of physi- and chemisorbed molecules on different adsorbents). Also spectra of a number of other small molecules adsorbed on C_{60} are presented and discussed.

2. IR SPECTROSCOPY OF SOME SMALL MOLECULES ADSORBED ON C_{60}

Application of IR spectroscopy, one of the major tools in surface science research, poses some difficulties in the study of adsorbates on graphite and carbon films, due to low transparency and reflectivity of these materials. This difficulty is not encountered in the case of C_{60} . Thin films of C_{60} are highly transparent, apart from few absorptions which will be addressed below.

The C_{60} films were prepared in a low-temperature adsorption cell, which served simultaneously for spectroscopic and adsorption studies[4]. The high surface area C_{60} was deposited onto a cooled central window, usually CsBr, kept at 77 K (liquid nitrogen), by evaporating small C_{60} crystals (99.95% pure) from a small tantalum crucible placed opposite to the window during deposition. At a sublimation temperature of 670 K, the deposition of the film was usually completed within about 30 min. The films were annealed for several

hours at 100-120 K to ensure their greater stability and reproducibility of results.

The vibrational modes of solid C_{60} can be subdivided into intermolecular and intramolecular vibrations. Detailed analysis both theoretical and experimental of the Raman and IR spectra exists in the literature. An extensive summary can be found in ref.[3]. Because of the molecular nature of solid C_{60} and the large difference in frequency between the inter- and intramolecular modes a decoupling of these two types of modes exists. The highest frequency phonon mode is at 60 cm^{-1} whereas the intramolecular modes have much higher frequencies.

Due to the high symmetry of the C_{60} molecule, of the 174 modes (most of them highly degenerated) only four fundamental transitions are allowed and active in the IR. In the spectrum of the films four strong and narrow absorption bands appear of 1430 cm^{-1} , 1183 cm^{-1} , 580 and 530 cm^{-1} . In addition, a series of weak bands is seen in the spectrum. These belong to other transitions which become partially allowed due to the presence of ^{13}C isotopes, combination bands and overtones, Figure 1.

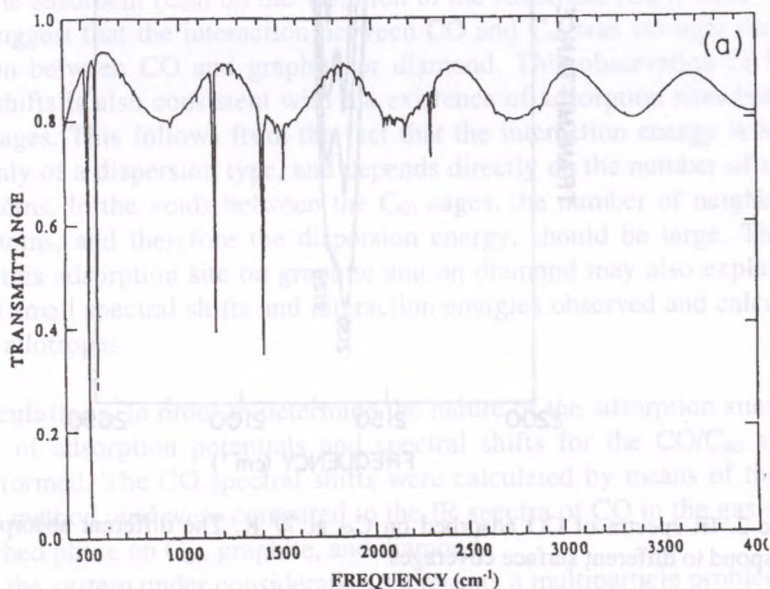


Figure 1. IR spectrum of C_{60} thin film

Spectrum of CO adsorbed on C_{60} . The spectrum of CO adsorbed at 77K on the C_{60} films clearly shows the presence of the above-mentioned four fundamentals of the substrate. In Figure 2 the absorptions of CO only are shown[4].

Two superimposed and well-resolved absorption bands are observed, positioned at $2135 \pm 1\text{ cm}^{-1}$ and at $2128 \pm 1\text{ cm}^{-1}$. The corresponding spectral shifts

from the gas-phase frequency (2143 cm^{-1}) are 8 and 15 cm^{-1} . During the initial stage of adsorption, the 2128-cm^{-1} band appeared first. Upon further adsorption, the intensity ratio of the two bands varied. When these systems were pumped at 77 K , the 2135-cm^{-1} absorption band disappeared first. It took over 2 h of pumping for the 2128-cm^{-1} absorption band to disappear from the spectrum.

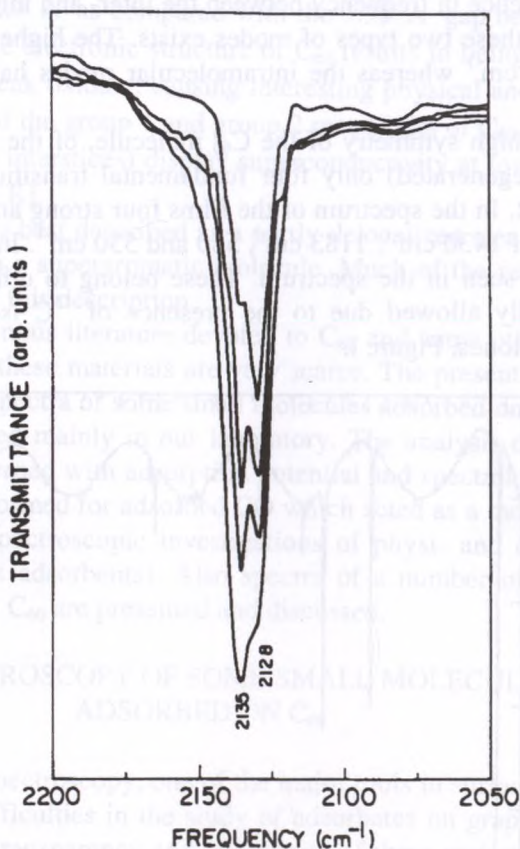


Figure 2. IR spectra of CO adsorbed on C₆₀ at 77 K. The different absorption bands correspond to different surface coverages

These results can be compared to previous measurements of the adsorption of CO on graphite and on diamond, by Tsidoni et al.[5] The IR spectrum of CO on the two allotropes showed one absorption band positioned at $2139 \pm 1\text{ cm}^{-1}$ for the graphite adsorbent, and one at $2144 \pm 1\text{ cm}^{-1}$ for the diamond adsorbent. The corresponding spectral shifts were -4 and $+1\text{ cm}^{-1}$. When the systems were pumped, it took only a few minutes at 77 K to desorb the CO from the two allotropes.

The appearance of two absorption bands, even at low coverages, in the IR spectra of adsorbed CO on C₆₀ suggests that CO was adsorbed on two different sites. This assumption is supported by the observation of different growth rates for the two absorption bands. It appears that the site which gave rise to the 2128-cm⁻¹ absorption band was the more energetic one, since its shift in frequency was larger and its desorption time was longer. The appearance of one absorption band in the IR spectra of adsorbed CO on the other allotropes, in contrast, shows that, for graphite and diamond, CO was adsorbed on only one site.

There are a number of possible adsorption sites on C₆₀. These include sites on the C₆₀ cage itself and sites between the relatively large C₆₀ cages. Since CO is a small molecule, it can readily penetrate into the voids between the C₆₀ cages. Diamond and graphite, because of their packed structures, have no such sites, thereby resulting in only one absorption band.

As stressed above, the adsorption of CO on C₆₀ also yielded larger spectral shifts, and longer desorption times, than the adsorption of CO on the other allotropes. Since the spectral shift is a measure of the perturbation of the surface field of the adsorbent (C₆₀) on the vibration of the adsorbate (CO), these observations suggest that the interaction between CO and C₆₀ was stronger than the interaction between CO and graphite or diamond. This observation of larger spectral shifts is also consistent with the existence of adsorption sites between the C₆₀ cages. This follows from the fact that the interaction energy is in this case mainly of a dispersion type, and depends directly on the number of neighboring atoms. In the voids between the C₆₀ cages, the number of neighboring carbon atoms, and therefore the dispersion energy, should be large. The absence of this adsorption site on graphite and on diamond may also explain the relatively small spectral shifts and interaction energies observed and calculated for these allotropes.

The Calculations. In order to determine the nature of the adsorption sites, calculations of adsorption potentials and spectral shifts for the CO/C₆₀ system were performed. The CO spectral shifts were calculated by means of the perturbation method, and were compared to the IR spectra of CO in the gas and in the adsorbed phase on C₆₀, graphite, and diamond.

Since the system under consideration represents a multiparticle problem, exact methods of adsorption potential calculations are difficult. Therefore, approximation methods have often been employed with quite good results. Low-temperature adsorption of CO on C₆₀ and other carbon allotropes is physical in nature; therefore potentials suitable for this type of adsorption were chosen. Adsorption potential of CO on C₆₀ was calculated by summing the dispersion and the repulsion potentials between the adsorbed molecule and each atom of

the adsorbent. In the calculations, the 6-exponential and the Lennard-Jones potentials were used.

Results were obtained for the fcc (100) and fcc (111) planes as well as for hcp (001) and hcp (111) structures. With the 6-exponential potential the total adsorption potential is given by

$$\phi_A = \phi_D + \phi_R \quad (1)$$

ϕ_D is the dispersion potential and ϕ_R the repulsion potential. The dispersion potential was calculated using the well-known Kirkwood-Muller expression, which is given as a sum of pair interactions of the adsorbed molecule and each atom of the adsorbent:

$$\phi_D = 6mc^2 \frac{\alpha_s \alpha_a}{\alpha_s / \chi_s + \alpha_a / \chi_a} \sum_i R_i^{-6} \quad (2)$$

Here subscript a refers to the adsorbate (CO molecule) and the subscript s to the C atom of the substrate, m is the mass of the electron, c the velocity of light, α_a and α_s the polarizabilities, and χ_a and χ_s the diamagnetic susceptibilities of the adsorbate and the C atom in C_{60} . For CO and C the numerical values of the different constants in the above equations are well known and appear in ref. [6]. The lattice sums $\sum R^{-6}$ were calculated by computer for different surface sites and crystallographic structures. The summation was performed over two planes, each plane contained 36 molecules. Due to the fast convergens of the sum, there was no need to extend the summation to additional planes.

The repulsion potential was calculated from

$$\phi_R = B \exp(-cR) = (B_s B_a)^{1/2} \exp\left[-\frac{(c_s + c_a)}{2} R\right] \quad (3)$$

The constants B and c were taken as geometrical and arithmetical means, respectively, of the corresponding constants for repulsion between the adsorbate molecules and the adsorbent atoms themselves. Reliable data exist for repulsion constants for CO in the gas phase and for crystalline CO. However, the constant B_s for repulsion between carbon atoms has to be calculated from the C_{60} intermolecular potential by equating the first derivative at minimum to zero. Additional numerical values of the different constants are given in ref.[6]

The second calculation was done by means of the L-J equation

$$\phi_{LJ} = -AR^{-6} + BR^{-12} \quad (4)$$

The A and B constants were taken as geometrical means of the corresponding values for attraction and repulsion between the adsorbate molecules

in the gas and the adsorbent atoms themselves. R is the distance between the adsorbed molecule and each carbon atom in C_{60} . The constants A and B for C_{60} and CO exist in the literature. The total adsorption potential ϕ_A is a sum of ϕ_L expressions.

C_{60} crystallizes in a fcc structure, however, an hcp structure is obtained if some impurities, or gases, are present during condensation of C_{60} vapors, which was the case in our experiments. The adsorption potential calculations were performed for the two structures. Two surface planes, the (100) and the (111), were chosen as adsorption planes on which a number of sites were selected. For the fcc (100) and the hcp (111) structures the sites were (1) the void space between four neighboring C_{60} molecules, (2) the void space between two neighboring C_{60} molecules, (3) the center of the hexagon on the C_{60} surface, and (4) the center of the pentagon on the C_{60} surface.

For the fcc (111) and hcp (001) surfaces the following sites were chosen for the calculations: (1) the void space between three neighboring C_{60} molecules; (2) the void space between two neighboring C_{60} molecules; (3) the center of the hexagon on the C_{60} surface; (4) the center of the pentagon on the C_{60} surface.

Spectral Shift Calculations. The spectral shifts were calculated for CO adsorbed at the different adsorption sites and surface faces of the two structures. This was done by using the perturbation method in which the adsorption potential acts as the perturbation Hamiltonian. In the calculation it was assumed that the center of the molecule remains at the equilibrium distance from the surface, and during the vibration, the perturbation oscillates as a result of small changes in the polarizability of the molecule with the change in the vibration coordinate.

Moreover, it was assumed that there was no interaction between the adsorbed molecules themselves (no lateral interaction) and also that there was no interaction between the internal modes and the vibration of the whole molecule with respect to the surface.

The total Hamiltonian of the adsorbed CO molecule is given by

$$H = H_a + H_s \quad (5)$$

Where H_a is the Hamiltonian of the anharmonic oscillator and H_s the perturbation due to the adsorbent. The energy levels are given by the general expression

$$W_n = W_n^a + W_n^s \quad (6)$$

where W_n^a represents the n energy level of the anharmonic oscillator and W_n^s the first- and second-order correction to the energy due to perturbation of the surface.

$$W_n^s = \int \varphi_n^a H_s \varphi_n^a dr + \sum_n \frac{\left[\int \varphi_n^a H_s \varphi_n^a dr \right]^2}{W_n^a - W_m^a} \quad (7)$$

here r is the vibration coordinate. The shift in frequency resulting from this procedure is given by

$$\Delta v = \left(\frac{B_0}{h\nu_0} \right) (\phi_A'' - 3a\phi_A') \quad (8)$$

where B_0 is the rotational constant of the molecule ($B_0 = 1.93 \text{ cm}^{-1}$), ν_0 the harmonic frequency of the oscillator ($\nu_0 = 2170.2 \text{ cm}^{-1}$), and a the anharmonicity constant [7]. For pure vibrational transition, in absence of rotation, which applies to our system $a = -1$, ϕ' and ϕ'' are the first and the second derivatives of the perturbing potential. Since the Lennard-Jones potential cannot be expanded in terms of the vibration coordinate of the adsorbate, spectral shifts for CO adsorbed at the different sites were calculated by means of the 6-exponential potential only. The spectral shift is given as a sum of contributions from dispersion and repulsion potentials. In the dispersion potential, the polarizability α_a is the property which changes with the vibration. For the differentiation of this potential, only α_a in the numerator was considered. The influence of the expansions of α_a in the denominator is negligible and therefore was considered constant.

$$\Delta v_{disp} = \frac{B_0 M}{h\nu_0} \left[\left(\frac{\partial^2 \alpha_a}{\partial r^2} \right) r_\epsilon^2 + 3 \left(\frac{\partial \alpha_a}{\partial r} \right) r_\epsilon \right] \quad (9)$$

where

$$M \equiv 6mc^2 \frac{\alpha_s}{\alpha_s / \chi_s + \alpha_a / \chi_a} \sum_i R_i^{-6}$$

The first and the second derivatives of α with respect to r , the internuclear distance, are known both from theoretical expressions and from experiment (Raman band cross section).

The contribution of the repulsion potential to the spectral shift was calculated by differentiating this potential with respect to the distance from the surface of the vibrating molecule:

$$\Delta v_{rep} = \frac{B_0}{h\nu_0} Bc \exp(-cR_\epsilon) \exp(cR_\epsilon) (c+3) \quad (10)$$

where B and c were defined in eq. 3.

As already mentioned the adsorption potentials and the spectral shifts were calculated for the CO molecule adsorbed on the fcc (100) and (111) and hcp

(100) and (111) structures of C_{60} . Detailed results are given in refs. [6], [8] - here selected results only will be shown. In Table 1, the numerical values are summarized: the equilibrium distance, the potential value at the minimum and the calculated spectral shift for both fcc (100) and hcp (111) structures. In Figures 3 and 4 are plotted the adsorption potentials as a function of the adsorbate distance from the surface.

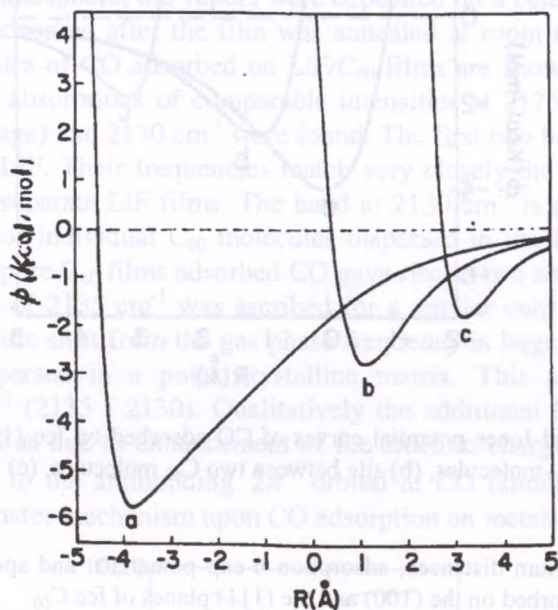


Figure 3. 6-exponential potential curves of CO adsorbed on fcc (100) plane of C_{60} : (a) site between four C_{60} molecules, (b) site between two C_{60} molecules, (c) site in the center of the hexagon

It is evident that the site of the lowest adsorption potential - 5.8 kcal/mol is the void space between four neighboring C_{60} molecules on the fcc (100) surface plane. On this site the CO molecule is located 3.8 Å below the surface plane (the surface plane is tangential to the outermost C_{60} molecules). For this configuration, the calculated spectral shift amounts to $\Delta\nu = -15.3 \text{ cm}^{-1}$. For CO adsorbed on the hcp (001) plane the calculated shift is -15.0 cm^{-1} . From the comparison of the calculated spectral shifts with the experimental ones, it is evident that the absorption band shifted by -15 cm^{-1} may be attributed to CO molecules adsorbed in the above-mentioned void spaces. The second band seen in the spectrum is shifted by -8 cm^{-1} from the gas phase absorption band gas value. It may be attributed to adsorption of CO between two C_{60} molecules on the different planes of the two structures. Since the evaporated C_{60} films are

composed of small crystalites all the adsorption sites pertinent to the above structures might be present.

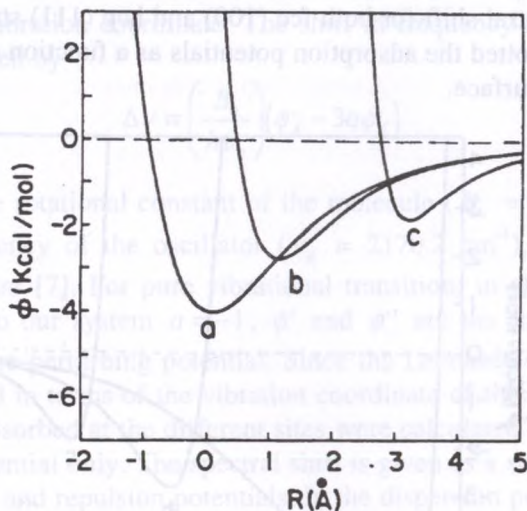


Figure 4. Lennard-Jones potential curves of CO adsorbed on fcc (111) of C_{60} : (a) site between three C_{60} molecules, (b) site between two C_{60} molecules, (c) site in the center of the hexagon

Table 1. Equilibrium distances, adsorption 6-exp potentials, and spectral shifts, calculated for CO adsorbed on the (100) and the (111) planes of fcc C_{60}

Adsorption site	Plane	Equilibrium distance, R_e (Å)	Potential ϕ_A (kcal/mol)	Spectral shift $\Delta\nu$ (cm^{-1})
void space between four C_{60} molecules	(100)	-3.8	-5.76	-15.3
void space between two C_{60} molecules	(100)	+1.1	-2.79	-9.2
on top of C_{60} molecule above the center of the hexagon	(100)	+3.2	-1.82	-6.3
void space between three C_{60} molecules	(111)	+0.1	-4.05	-13.5
void space between two C_{60} molecules	(111)	+1.1	-2.91	-9.1
on top of C_{60} molecule above the center of the hexagon	(111)	+3.2	-1.85	-6.4

Spectra of CO adsorbed on LiF/C₆₀ and NaCl/C₆₀. The above results lead to an attempt to obtain spectra of CO on individual C₆₀ molecules[9]. Films of LiF and NaCl with embedded C₆₀ molecules were prepared by simultaneous deposition of the two materials from two separate sublimation sources. In a low temperature cell, a tantalum basket for the salt deposition and a crucible for the C₆₀ powder were employed. The films were prepared by operation of the two sources in a He atmosphere, the vapors were deposited on a cold CsBr window (77K). CO was adsorbed after the film was annealed at room temperature. In Figure 5. IR spectra of CO adsorbed on LiF/C₆₀ films are shown for different coverages. Three absorptions of comparable intensities at 2175, 2162-53 (depending on coverage) and 2130 cm⁻¹ were found. The first two bands are due to CO adsorbed on LiF. Their frequencies match very closely the frequencies of CO adsorbed on separate LiF films. The band at 2130 cm⁻¹ is ascribed to CO adsorbed on top of individual C₆₀ molecules dispersed in the LiF matrix. As shown above, on pure C₆₀ films adsorbed CO gave rise to two absorption bands of which the one of 2135 cm⁻¹ was ascribed for a similar configuration. This would mean that the shift from the gas phase frequency is larger when the C₆₀ adsorbent is dispersed in a polar crystalline matrix. This additional shift amounts to 5 cm⁻¹ (2135 - 2130). Qualitatively the additional frequency shift may be explained as due to enhancement of the electron charge transfer from the C₆₀ molecule to the antibonding 2π* orbital at CO (similarly to the accepted charge-transfer mechanism upon CO adsorption on metals).

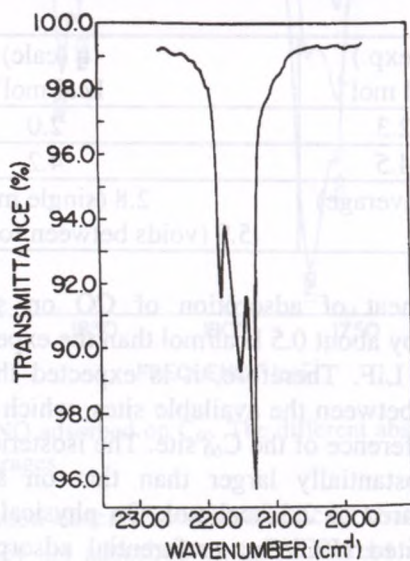


Figure 5. IR spectra of CO adsorbed on simultaneously deposited LiF/C₆₀ film spectrum (T = 77 K)

The enhancement of the electron charge-transfer maybe caused by polarization of the C_{60} molecules by the electrostatic field present on the LiF surface. As a result of surface relaxation in the alkali-halide crystals, the negative ions in the surface are displaced outwards. The displacement produces an appreciable electrostatic dipole. The direction of the dipole is such that the change in electron charge distribution in C_{60} will favor electron charge transfer to the adsorbate.

The results obtained with the mixed NaCl/ C_{60} films are strikingly different. Absorption bands due only to CO adsorbed on NaCl were seen: one dominant band at 2155 cm^{-1} and a very weak shoulder at 2173 cm^{-1} , similar to the very well known spectra of CO adsorbed on pure NaCl films[10]. No absorptions due to CO on C_{60} were seen, except at higher surface coverages above $\theta = 0.30$ a very faint band at 2130 cm^{-1} appeared. To explain the different behaviour of the two systems towards adsorption of CO, the heats of adsorption of CO on C_{60} , LiF and NaCl were calculated and measured experimentally.

For CO on LiF and on C_{60} the heats of adsorption were obtained by calculating the adsorption potentials and by measuring the isosteric heats of adsorption spectroscopically[9]. For CO on NaCl both theoretical and experimental results exist and appear in the literature[10].

The numerical values of the heats of adsorption are given in Table 2.

Table 2. Experimental and calculated isosteric heats of adsorption of CO on various adsorbents

Adsorbents	q(exp.) kcal mol ⁻¹	q (calc) kcal mol ⁻¹
CO/LiF	2.3	2.0
CO/NaCl	4.5	4.2
CO/ C_{60}	4.0 (average)	2.8 (single molecule) 5.9 (voids between four molecules)

The calculated heat of adsorption of CO on single C_{60} molecules, 2.8 kcal/mol is larger by about 0.5 kcal/mol than the experimental isosteric heat of adsorption on the LiF. Therefore, it is expected that the CO molecules should be distributed between the available sites, which do not differ much in energy, with some preference of the C_{60} site. The isosteric heat of adsorption of CO on NaCl is substantially larger than that on single C_{60} molecules: 5.5 kcal/mol as compared to 2.8 kcal/mol. On physical adsorption of CO on simultaneously deposited NaCl/ C_{60} , preferential adsorption of CO on NaCl should be obtained. Only when most of the adsorption sites on NaCl are occupied is a small fraction of the CO molecules adsorbed on C_{60} .

Spectrum of NO adsorbed on C₆₀. The spectrum of NO adsorbed on C₆₀ at 77K is shown in Figure 6. Two pairs of superimposed absorption bands are observed. The frequencies of the more intense doublet are 1858 cm⁻¹ and 1765 cm⁻¹ and the corresponding shifts from the gas phase frequency are 2 and 23 cm⁻¹. The frequencies of the less intense doublet are 1853 and 1755 cm⁻¹ and the corresponding spectral shifts are 7 cm⁻¹ and 33 cm⁻¹. On adsorption the two components of each doublet appeared simultaneously. When the coverage was increased the intensity ratio of the two components of each doublet remained constant. The intensity ratio of the doublets, however, did not remain constant, and at low coverages, only the less intense doublet was observed.

NO exists in the gas phase as single molecules, and only a very small concentration of dimers is present. In the solid and liquid phases, however NO exists mainly as dimers. In the adsorbed state NO dimers were found on graphite and on diamond.

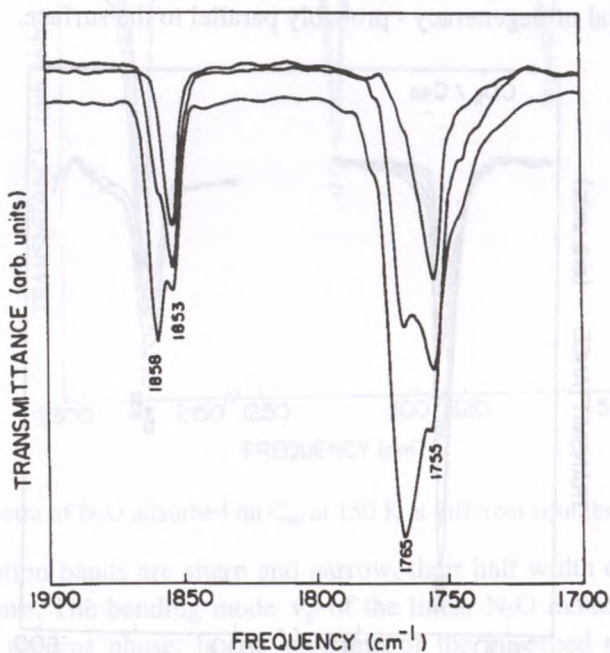


Figure 6. IR spectra of NO adsorbed on C₆₀. The different absorption bands correspond to different surface coverages

The above described observations also indicate that the NO dimers are adsorbed on C₆₀, and they are adsorbed on two different sites. The simultaneous appearance of the two components of each doublet indicates that the doublet belongs to a single dimer and not to a single NO molecule adsorbed on two

different sites. The different growth rates of the doublets also indicates that NO dimers are adsorbed on two different sites on C_{60} .

Spectrum of CO_2 adsorbed on C_{60} . On adsorption of CO_2 two absorption bands are obtained, one at a frequency 2328 cm^{-1} ascribed to the antisymmetric ν_3 stretching vibration and a second as a doublet which components were 654 and 652 cm^{-1} Figure 7. The latter band is assigned to the degenerate (in gas phase) ν_2 bending mode. The ν_3 band is sharp and narrow. On adsorption and on desorption, the two components of the doublet appeared and changed in intensity simultaneously. The splitting of the doublet amounted to 2 cm^{-1} , the two components were shifted by 15 and 13 cm^{-1} from the Q-band of the CO_2 at 667 cm^{-1} in the gas. The splitting of ν_2 into a doublet is an important feature of the spectrum. Its appearance maybe explained either by adsorption of CO_2 molecules on two different sites or by adsorption on one site in a way which leads to removal of degeneracy - probably parallel to the surface.

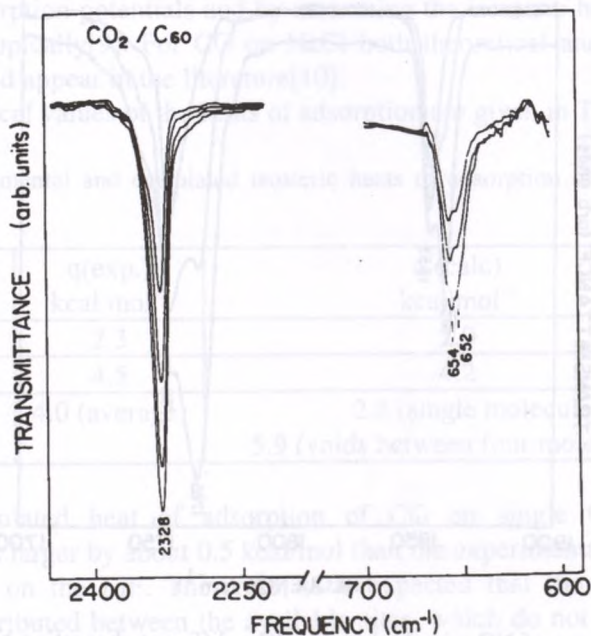


Figure 7. IR spectra of CO_2 adsorbed on C_{60} at 150 K and at different equilibrium pressures

The fact that the two components of the doublet changed simultaneously on adsorption and on desorption indicates that the second assumption, namely the removal of degeneracy is a more plausible one. Moreover, if the doublet was

due to the existence of two adsorption sites, not only the ν_2 band, but also the ν_3 would be expected to appear as a doublet.

Upon adsorption of CO_2 on graphite and diamond films, somewhat different results were obtained. Both spectral shifts and the shape of the bands were different. The splitting of the doublet in the system $\text{CO}_2/\text{graphite}$ was 5 cm^{-1} . In the $\text{CO}_2/\text{diamond}$ system the ν_2 was not observed.

Spectrum of N_2O adsorbed on C_{60} . The N_2O molecule has three normal modes. They are allowed and active in the IR. Indeed, all of them appear in the spectra of adsorbed N_2O , which are shown in Figure 8.

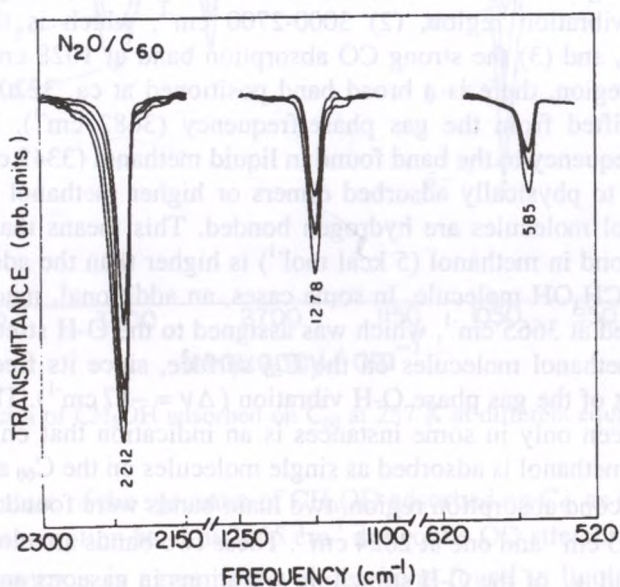


Figure 8. IR spectra of N_2O adsorbed on C_{60} at 150 K at different equilibrium pressures

The absorption bands are sharp and narrow, their half width do not change with temperature. The bending mode ν_2 of the linear N_2O molecule is doubly degenerate in the gas phase. In the spectrum of the adsorbed molecule, this vibration appears as a single band shifted by 4 cm^{-1} to lower frequency. The ν_1 is also shifted to lower frequency by 7 cm^{-1} and the ν_3 by 12 cm^{-1} . In some respects the adsorbed N_2O molecules behaved similarly to CO_2 . The absorption bands were sharp and narrow, their half widths did not change with temperature, so that rotation of the molecule in the adsorbed state is excluded. From the fact that each of the three modes of vibration appeared as a single absorption band, it was concluded that N_2O molecules were adsorbed on one site only, in

an orientation which does not remove the degeneracy of the bending ν_2 mode, that is normal to the surface. In Ref. [11], the frequencies and the shifts of the different vibration are listed.

Spectra of CH₂OH and CH₃OD adsorbed on C₆₀. The spectra of methanol and deuterated methanol (CH₃OD) adsorbed on C₆₀ were recorded on adsorption and on desorption [12], at different temperatures (273, 263 and 257 K) and different equilibrium pressures, Figures 9, and 10. The peak frequencies of the absorption bands of the adsorbates as well as those of the gas and liquid phases are given in Ref. [12]. The IR spectrum of adsorbed CH₃OH can be divided into three main regions: (1) 3700-3000 cm⁻¹, which is generally assigned to the O-H stretching vibration region, (2) 3000-2700 cm⁻¹, which is the C-H region (stretching), and (3) the strong CO absorption band at 1028 cm⁻¹. In the high-frequency region, there is a broad band positioned at ca. 3220 cm⁻¹, which is strongly shifted from the gas phase-frequency (3682 cm⁻¹). It is, however, nearer in frequency to the band found in liquid methanol (3342 cm⁻¹). This band is assigned to physically adsorbed dimers or higher methanol clusters, where the methanol molecules are hydrogen bonded. This means that the energy of hydrogen bond in methanol (5 kcal mol⁻¹) is higher than the adsorption energy of a single CH₃OH molecule. In some cases, an additional, much weaker band was observed at 3665 cm⁻¹, which was assigned to the O-H stretching vibration of single methanol molecules on the C₆₀ surface, since its frequency is quite close to that of the gas phase O-H vibration ($\Delta\nu = -17$ cm⁻¹). The fact that this band was seen only in some instances is an indication that only a very small fraction of methanol is adsorbed as single molecules on the C₆₀ surface.

In the second absorption region, two main bands were found: an asymmetric band at 2935 cm⁻¹ and one at 2824 cm⁻¹. These two bands are close in frequency to the ν_5 and ν_2 of the C-H stretching vibrations in gaseous and liquid methanol. A shoulder at 2970 cm⁻¹ could be identified on the asymmetric absorption band at 2335 cm⁻¹. The band and the shoulder can be due either to the two components of the ν_5 vibration or to Fermi resonance between C-H stretching vibrations, ν_5 and ν_2 and the overtone of the CH₃ deformation vibration. Similar bands were found on carbon films at 2960 cm⁻¹ and 2840 cm⁻¹. No absorption bands in the ν_3 (CH₃ deformation vibration) and ν_8 (OH bending vibration) regions were found.

A strong absorption band was detected at 1028 cm⁻¹, which is assigned to the C-O, ν_4 stretching mode of methanol physisorbed on C₆₀. On carbon films a band of 1030 cm⁻¹ was found and similarly, was assigned to physisorbed methanol in micropores. On desorption, while heating the film to room temperature or higher (340 K) the above band decreased greatly in intensity and

shifted to 1024 cm^{-1} , while the other bands in the O-H and C-H stretching regions could barely be seen. From this it can be inferred that a small fraction of methanol is either chemisorbed or adsorbed at higher energy sites such as the voids between C_{60} molecules.

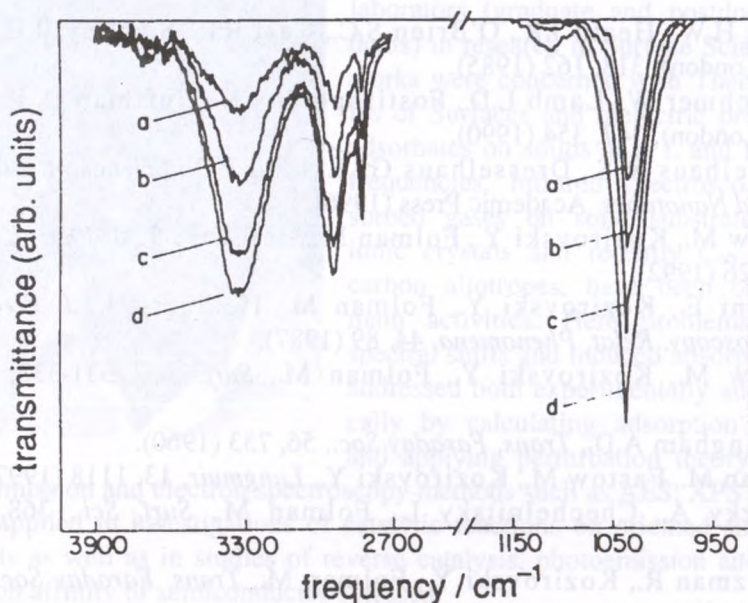


Figure 9. IR spectra of CH_3OH adsorbed on C_{60} at 257 K at different equilibrium pressures

The main feature of the spectrum of CH_3OD adsorbed on C_{60} as compared to CH_3OH , is the absorption band at 2465 cm^{-1} due to the OD stretching ν_1 vibration. This frequency is in agreement with the band found in liquid CH_3OD at 2492 cm^{-1} , and indicates that similarly to CH_3OH the CH_3OD molecules are adsorbed as hydrogen bonded clusters. Adsorbed CH_3OD gave rise to two bands in the CH stretching region and a band at 1028 cm^{-1} due to CO, similarly to adsorbed CH_3OH .

3. SUMMARY

The paper reviews briefly recent work on IR spectra of a number of small molecules adsorbed on C_{60} . Absorption spectra of adsorbed CO, NO, CO_2 , N_2O and CH_3OH are shown and discussed. In addition to experimental results, calculations of adsorption potentials and spectral shifts for adsorbed CO on different sites and surface planes on the C_{60} films are presented. In some instances

comparison was made with corresponding spectra of the adsorbates on the other two carbon allotropes: graphite and diamond.

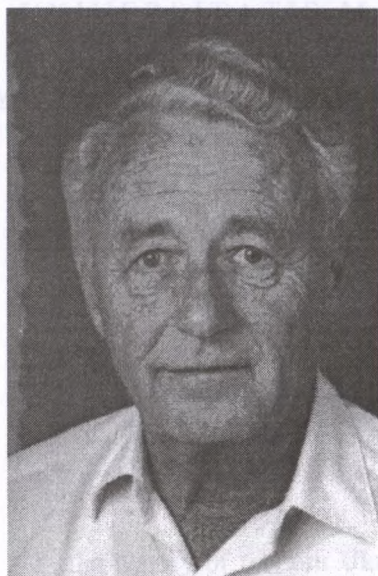
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CURRICULUM VITAE

Prof. Mordechai Folman. Professor Emeritus, Born in Łódź, Poland 1923. After the 2nd world war studied Chemical Engineering at the Łódź Polytechnic. In 1950 received his Chem. Eng. and M. Sc. Degrees. In the same year emigrated to Israel. In 1955 received the D. Sc. Degree at the Technion – Israel Inst. of Technology and in 1958 the Ph. D. Degree at the University of Cambridge (England).

On the Technion Faculty since 1951. From 1967 full Professor in Physical Chemistry. Chairman, Department of Chemistry 1976-1980. Since 1978 Head



of Surface Science Center. 1982-85 Head of the Solid State Institute at the Technion. Yaacov Dori Chair in Sciences.

Over the years was involved with his collaborators (graduate and postdoctoral students) in research in Surface Science. Early works were concerned with Thermodynamics of Surfaces and dielectric properties of adsorbates on solids at r. f. and microwave frequencies. Infrared spectroscopy of adsorbed gases on solid substrates, mainly ionic crystals and recently C_{60} and other carbon allotropes, have been one of his main activities. Here problems such as spectral shifts and induced absorptions were addressed both experimentally and theoretically by calculating adsorption potentials and applying perturbation theory. Electron

field emission and electron spectroscopy methods such as AES, XPS and EELS were applied in investigations of catalytic reactions on oriented single metal crystals as well as in studies of reverse catalysis, photoemission and negative electron affinity of semiconductor surfaces.

