OPTICAL VIBRATION SPECTRA OF C_{24} AND C_{48} CAGE CLUSTERS AND SIMPLE CUBIC FULLERITE

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An analysis of the structure of a new carbon phase, namely, 'cubic graphite", has been carried out by optical spectroscopy and computer simulation. Computer simulation results of IR and Raman spectra of carbon cage clusters C_{24} and C_{48} are presented. Calculations have been performed by the spin-restricted Hartree–Fock (RHF) method with the 6-31G(d) basis set. We present the experimental Raman spectra of samples of carbon crystals of the cubic system referred to as cubic graphite in the frequency range 50–3500 cm^{-1}, where the new bands of carbon materials were observed in the frequency range 600–800 cm^{-1}. The analysis of the most intense calculated normal vibrations and the new experimentally detected bands has shown that the location of experimental bands correlates well with that for the theoretically calculated spectrum of cluster C_{24}.

1. Introduction

In recent years, it has been shown [1–4] that carbon fullerenes and inorganic cage clusters of a fullerene-like morphology can be considered as the structural units of both molecular crystals and crystal lattices with sp^2, sp^3, and mixed $sp+sp^2+sp^3$ bonds. At the sites of these lattices, clusters are located, and the size of lattice voids is equal to that of clusters; like aluminum silicates and other minerals (zeolites), the crystals are nanoporous. Clusters of semiconductor compounds $A^{IV}B^{IV}$, $A^{III}B^{V}$, $A^{IV}B^{VI}$ in particular, BN, SiC, and ZnO, are of particular interest. It was shown earlier that these compounds are susceptible to the formation of fullerene-like cage structures [5]. The search, synthesis, and investigation of these clusters and crystals composed of them represent one of the most promising trends of modern nanomaterials science. The aim of the present work is to study the theoretical foundations of the development of new nanomaterials, specifically, their stability, electronic structure, optical vibrational spectra, and other physical properties of hypothetical structures and structures that have been synthesized. In the first stage of works in this direction, the investigation of the structural units of fullerite cluster crystals, which we called "crystal-forming clusters", was performed by methods of computational physics [3]. In the formation of a crystal, these clusters are polymerized by faces and provide the transformation of all sp^2 electronic configurations of a cluster to the sp^3 type configuration of the crystal.

The structure of zeolite-like crystals as crystal lattices with fullerene molecules located at their sites that are polymerized by faces was predicted in [1, 6]. A number of cubic and other lattices were proposed: simple cubic fullerite-C_{24} (SCF-C_{24}), body-centered cubic fullerite-C_{24} (BCCF-C_{24}) [7] *et al.* Only cage clusters of non icosahedral symmetry must be structural units of crystals with a cubic lattice. A C_{24} fullerene molecule was selected as a structural unit, because it is the smallest of polyhedra with the number of faces (six squares and eight hexagons) sufficient for the formation of cubic lattices, in which C_{24} molecules are bound with one another by covalent bonds, which are formed between adjacent square faces during the copolymerization (Fig. 1). The parameters of C_{24} molecule were determined in [7]. These are the T_h symmetry, energy of atomization of an atomic pair $E_a = 11.875$ kkal/mol, lengths of bonds shared by two hexagons and a hexagon-square, which are equal to $a_{6;6} = 0.138$ and $a_{6;4} = 0.1503$ nm, respectively.

The parameters of proposed SCF-C_{24} are similar to the parameters of "cubic graphite" [8]. The formation of this phase was recorded in [9]. It was shown that it has cubic symmetry, lattice constant $A = 0.5545$ nm, density of 2.80 g/cm^3, and number of atoms per unit cell $Z = 24$. More recently, a mixture of different carbon modifications, one of which can be identified as "cubic graphite", was obtained in [10]. In 2002, fullerite, whose parameters coincided with parameters of "cubic graphite", was synthesized in [11].

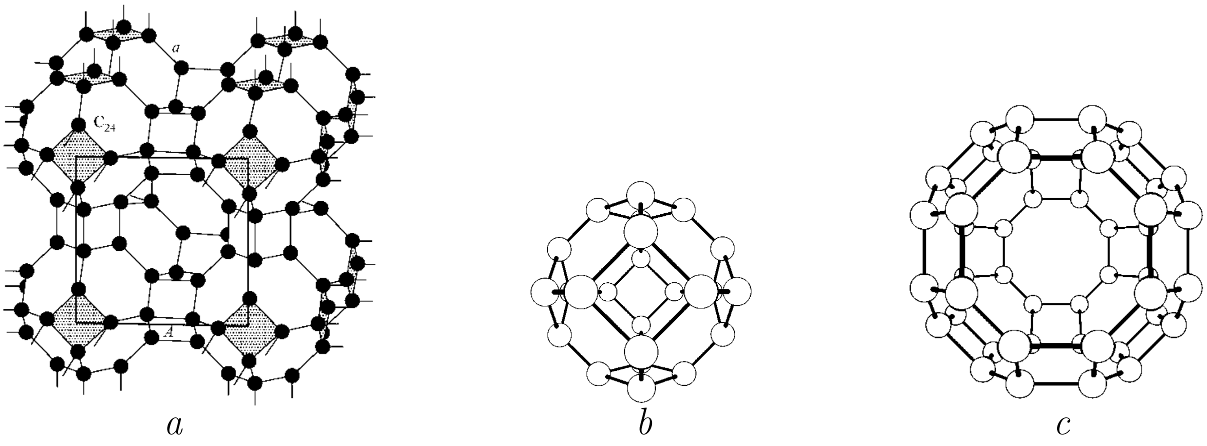

Fig. 1. Simple cubic lattice of SCF-C_{24} [7] (*a*) and carbon cage clusters C_{24} (*b*) and C_{48} (*c*)

The authors of [7], on the basis of an analysis of X-ray diffraction patterns of samples obtained by them and works of other authors, concluded that the structure of "cubic graphite" is SCF-C_{24}. In [12], computations of the total energy of SCF-C_{24} were performed by the full-potential linearized augmented plane wave method (FLAPW) [13] without optimization of the structure. These calculations indicate that SCF-C_{24} is a stable carbon phase, because the dependence of the total energy on the length of the bond a_{CC} is close to that for diamond and has a minimum. As in diamond, all the carbon atoms in SCF-C_{24} are bound by sp^3 hybridized bonds. Like zeolites, the SCF-C_{24} structure contains two-dimensional lattices of cylindrical nanopores with the diameter $D = 0.41$ nm and can be used as molecular sieves.

In the present work, an analysis of the structure of "cubic graphite" was performed on the basis of calculated optical vibrational spectra of carbon cage clusters [5, 14, 15] and experimental Raman spectra of samples of hypothetical "cubic graphite". The aim of the work is to substantiate the structure of "cubic graphite", which was established earlier by XRD and theoretical computations. The possibility of extending the results of simulation of isolated clusters to solid-state samples was also investigated.

2. Results and Discussion

Samples of "cubic graphite" were prepared by A. Smolyar [11]. These are opaque carbon crystals with cubic symmetry ($A = 0.56$ nm, density of 2.78 g/cm^3, hardness of 1–5 GPa) which are likely to be composed of carbon cage clusters.

At the Department of Experimental Physics of the Physical Faculty of the Shevchenko Kyiv National University, the Raman spectra of "cubic graphite" samples were recorded on an automated spectral complex based on a DFS-24 spectrometer in the frequency range 50–3500 cm^{-1} under the excitation with argon-laser radiation ($\lambda_L = 488.0$ and 514.5 nm).

The equilibrium geometry, electronic structure, and theoretical vibrational spectra (IR absorption spectra and Raman scattering spectra) of C_{24} and C_{48} clusters were also calculated and investigated. For the most characteristic modes, the shapes of normal vibrations were analyzed. Clusters C_{24} and C_{48} are systems with a closed shell (the number of electrons is even, and all their spins are coupled). For this reason, the spin-restricted Hartree–Fock method and the Pople split-valence basis set of wave functions with polarization of *d*-functions (RHF/6-31G(d)) were used in calculations. The geometry of the structure was optimized by the steepest descent method. The calculation of IR absorption spectra and Raman spectra was performed in the harmonic oscillator approximation, within the framework of the method and the basis set that were used in the previous optimization of the structure of the clusters. The calculation of the intensities of vibrations in the IR absorption spectra was performed within the framework of the dipole approximation. The intensities of vibrations in the Raman spectra were determined by the numerical differentiation of the polarization tensor using the Komornicki method [16]. To account for the overestimation of the frequency of vibrations as a result of the system error, which is characteristic of calculations by the Hartree–Fock method, the values on the axis of the frequency spectrum were multiplied by an empiric coefficient of 0.8929 [17].

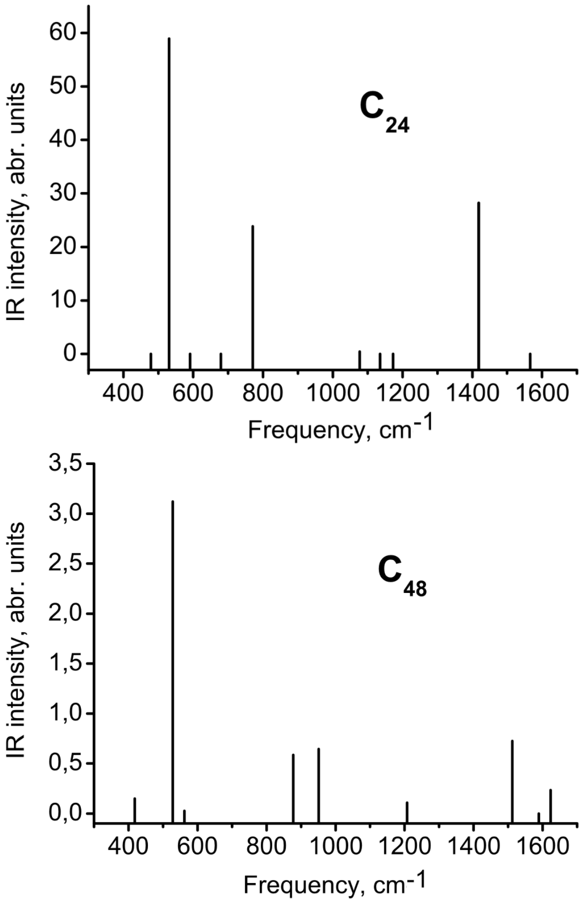

Fig. 2. IR spectra of clusters C_{24} and C_{48}

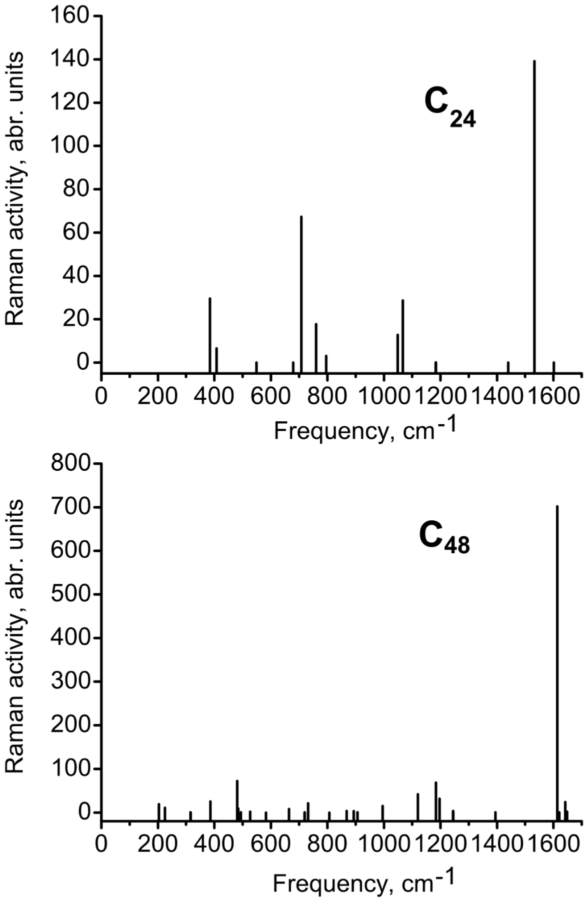

Fig. 3. Raman spectra of clusters C_{24} and C_{48}

In the IR absorption spectra of clusters C_{24} and C_{48}, the most intensive peaks of vibrations are in the long-wave area of the spectrum (Fig. 2). With increase of the frequency, the vibrations transform to radially tangential and then to tangential vibrations. For C_{24}, we observed the most intensive peaks at 531 cm^{-1} and 1418 cm^{-1}. For C_{48}, we recorded a pronounced peak at 528 cm^{-1} and three peaks of a smaller intensity at 877 cm^{-1}, 951 cm^{-1}, and 1512 cm^{-1}. The character of location of the most intensive modes (that were obtained by the authors) correlate with those for C_{24} and C_{48}. For both clusters, the peaks at 531 cm^{-1} for C_{24} and at 528 cm^{-1} for C_{48} are related to radial shifts of atoms under the vibration of the whole molecule. The stretching and the shortening of bonds and a deformation of corners occur. The mode at a frequency of 877 cm^{-1} is related to the radially symmetric vibrations of two diametrically opposite octagons in antiphase. The types of vibrations at a frequency of 1418 cm^{-1} for C_{24} and at frequencies of 951 cm^{-1} and 1512 cm^{-1} for C_{48} are tangential and similar.

The analysis of the calculated Raman spectra (Fig. 3) enabled us to establish that, in the spectra of clusters C_{24} and C_{48}, the most intensive vibrations are located in the short-wave region of the spectrum, namely, at 1543 cm^{-1} and 1642 cm^{-1}, respectively, and correspond to the mode with tangential shifts of all atoms. This peak can be compared with the experimentally determined characteristic vibration of double bonds of C=C [18]. The so-called "breathing" mode was observed in the Raman spectra of C_{24} and C_{48}, at 708 cm^{-1} and 481 cm^{-1}, which is related to the fully symmetric radial vibrations of the clusters, whose intensity is smaller than that for the tangential shear mode of atoms.

In Raman spectra, the vibrational modes of C_{48} are shifted to the region of lower frequencies in comparison with the peaks for C_{24} in accordance with the increase in the macromolecule mass. However, in the IR absorption spectra, the shifts of peaks of the most intensive tangential vibrations in the direction of lower frequencies are not observed. This may be associated with the size effect [19], i.e., the shortening of the bonds in cluster C_{48} against those for cluster C_{24} and the corresponding shift of peaks of vibrations in the direction of higher frequencies.

After the calculation of the optical vibrational spectra of carbon cage clusters, we obtain the possibility of comparing the calculated Raman spectra with the experimental ones for samples of "cubic graphite", which is likely to be composed of carbon cage clusters (Fig. 4).

The general theory of harmonic vibrations of crystals [20] considers a crystal, in each elementary cell of which there are n particles, and the size of the periodicity includes $N = L^3$ unit cells. The theory enables one to classify main vibrations of the crystal for any number of nonequivalent atoms in a cell. In connection with the character of forces that act between particles, it is reasonable to isolate individual groups of atoms, which can be considered as structural units of the crystal. Complex ions and individual molecules in molecular atoms can be such groups [18]. In zeolite-like crystals, shell clusters can be such groups. In this case, the normal vibrations are divided into external and internal ones. The external vibrations are vibrations of clusters relative to one another. The internal vibrations are vibrations of atoms inside clusters. In the case where clusters are integrated into a crystal, the perturbation of intramolecular vibrations by the field of the crystal lattice, i.e., static and dynamic splitting, arises. The static field of the crystal leads to a shift of frequencies and a change in the rules of selection for intramolecular vibrations. As a result, some forbidden frequencies can become active, and the degenerate frequencies can split. The resonant interaction of equal vibrations of molecules in a unit cell leads to the splitting of frequencies. In this case, the number of components of the split line cannot exceed the number of molecules in the unit cell. Moreover, the rule of selection may be violated in the crystal. Forbidden lines appear as a result of the excited vibrational state of the crystal at an increased temperature. Furthermore, as a result of thermal effects, the broadening of lines must occur. The presence of impurities and vacancies in a real crystal leads to the breakdown of translational invariance and, correspondingly, to the violation of the quasimomentum conservation law in the process of scattering.

As a result of the foregoing, in comparison with the theoretical spectrum of the cluster in the main state, the formation of additional lines, smearing of lines, and shifts of frequencies must be observed in the spectrum of the real crystal. In the low-frequency region of the spectrum, bands that correspond to vibrations of the crystal lattice must appear. In the case where clusters C_{24} integrate into a crystal, double sp^2 bonds are disrupted with the formation of hybridized sp^3 bonds between atoms of neighboring clusters. Finally, all carbon atoms in fullerite, as in the case of diamond, are bound by sp^3 hybridized bonds. In this case, in the Raman spectrum, the absence or noticeable weakening of the line at 1543 cm^{-1}, which is connected with a characteristic vibration of double bonds C=C, is expected.

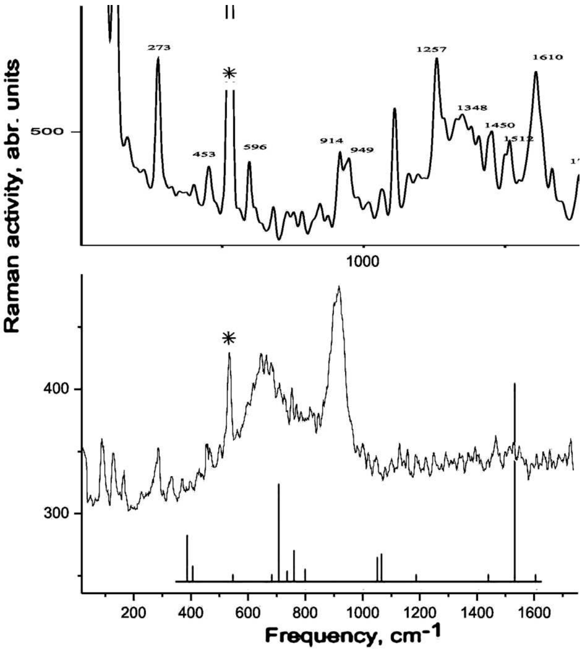

Fig. 4. Raman spectra of "cubic graphite" and cluster C_{24}, the initial material (soot, at the top). Lines of laser plasma are marked with asterisk

The comparison of the obtained Raman spectra of the initial material (carbon black) with the spectra of various carbon-graphite materials available in the literature showed that, along with the known characteristic bands, new rather intensive bands of carbon-graphite materials are observed in the frequency range 600–800 cm^{-1}. For the interpretation of the nature of these bands, the analysis of the relative position of vibrational bands of the spectra of predicted carbon clusters and the known phases of carbon materials that the authors calculated theoretically and their further comparison with experimental spectra is used. It was established that the character of location of experimental bands correlates well with that for the theoretically calculated spectrum of cluster C_{24}, which has intense vibrational peaks in this range, among which the peak at 708 cm^{-1} related to the totally symmetric radial vibrations of the cluster is the most characteristic. As would be expected, the line at 1543 cm^{-1}, which is related to the characteristic vibration of double bonds C=C, is absent in the spectrum. In the low-frequency region 100–200 cm^{-1}, the well-defined bands assigned to vibrations of the crystal lattice appeared. We can assume that the investigated sample contains carbon cage clusters C_{24}.

3. Conclusions

The Raman spectra of "cubic graphite" have been experimentally obtained. New fairly intense bands are identified for carbon materials in the frequency range 600–800 cm^{-1}. Raman spectra, IR absorption spectra, and the corresponding normal vibrations of carbon cage clusters C_{24} and C_{48} have been calculated by the *ab initio* Hartree–Fock method. Cluster C_{24} has intense vibrational peaks in the frequency range 600–800 cm^{-1}, among which the peak at 708 cm^{-1}, related to the totally symmetric radial vibrations of the cluster, is the most characteristic. The analysis of the most intense calculated normal vibrations and new experimentally detected bands has shown that the character of location of experimental bands correlates well with that for the theoretically calculated spectrum of cluster C_{24}. Based on the earlier obtained results of X-ray studies, we can assume that the structure of "cubic graphite" is a simple cubic fullerite SCF-C_{24}. The calculated spectra of the cage clusters can be used to interpret the experimental spectra of new synthesized nanostructures.

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ОПТИЧНІ КОЛИВАЛЬНІ СПЕКТРИ КАРКАСНИХ КЛАСТЕРІВ C_{24}, C_{48} І ПРОСТОГО КУБІЧНОГО ФУЛЕРИТА

Л.І. Овсяннікова, А.П. Науменко, В.В. Картузов, А.С. Смоляр

Резюме

Проведено аналіз структури нової фази вуглецю "графіт кубічний" методами оптичної спектроскопії і комп'ютерного моделювання. Наведено результати комп'ютерного моделювання ІЧ і КР спектрів каркасних вуглецевих кластерів C_{24} і C_{48}. Обчислення проведено у межах обмеженого по спіну методу Хартрі–Фока з набором базисних функцій 6-31G(d). Також наведено отримані експериментальні спектри комбінаційного розсіяння зразків кристалів вуглецю кубічної сингонії – "графіту кубічного", у діапазоні частот 50–3500 $см^{-1}$, де спостерігаються нові для вуглецевих матеріалів смуги у діапазоні частот 600–800 $см^{-1}$. Аналіз найбільш інтенсивних обчислених нормальних коливань і нових експериментальних смуг показав, що характер розміщення експериментальних смуг добре співвідноситься з теоретичним обчисленим спектром кластера C_{24}.