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Bulk and surface dynamics of graphite with the bond charge model

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The bond charge model (BCM), originally designed by Weber for the dynamics of tetrahedrally coordinated semiconductors, is shown to be applicable, with minor adjustments, to sp^2 configurations. Calculations for the bulk and surface dynamics of graphite, based on a comparatively small number of adjustable parameters (five or six), are shown to be in excellent agreement with recent inelastic helium atom scattering data and high-resolution electron-energy-loss spectroscopy. The parameter transferability to other forms of sp^2-bonded carbons is discussed with the indication that BCM is easily applicable to large structures (e.g., giant fullerenes) presently inaccessible to *ab initio* methods, with a comparatively modest computational effort.

I. INTRODUCTION

The successful application of the bond charge model (BCM) to the dynamics of π-bonded chains in the Si(111) 2×1 surface[1] has posed the question whether BCM applies to nontetrahedrally bonded systems, e.g., sp^2-bonded structures such as graphite[2] and fullerenes. Recently, we have shown that this model works very well for the fullerene C_{60}.[30] Here we show that BCM, with minor modification, is suitable for describing the dynamics of graphite layers.

Good and transferable models are often required to cover an area still inaccessible to *ab initio* methods: e.g., this would be the case of the giant fullerene architectures, composed of several hundred atoms, where BCM-like models yield a reliable prediction of vibrational spectra, provided the model is transferable. Moreover, a model such as the BCM, that includes the effects of the electronic degrees of freedom, can often be useful even for systems that can actually be treated by *ab initio* approaches as well. A good model calculation, in fact, can often provide reliable information that is indeed complementary to that obtainable from more sophisticated methods. Let us start from graphite, the prototype of sp^2-bonded materials, and consider both its bulk phonons (to compare with the existing force-constant models) and the (001) surface dynamics (to compare with the experimental data where surface-sensitive probes have been used).

Several models[4-9] have been proposed in recent years for the bulk lattice dynamics of graphite, which give good agreement with the measured dispersion relations in the low-lying region across the Brillouin zone, and with the optical frequencies at the zone center. The most recent and popular models reproducing at least all the measured frequencies at the Γ point are by Maeda-Horie (HM) (eight parameters) (Ref. 7) and by Al-Jishi and Dresselhaus (AJD) (20 parameters).[8] Both are simple Born–von-Karman models, employing, respectively, second-neighbor and fourth-neighbor radial and tangential noncentral force constants.

Surface phonons on the (001) graphite surface have been investigated by De Rouffignac, Alldredge, and De Wette[10] by means of the slab method. Their calculation for a 13-layer slab, published in 1981, was performed on the basis of a modified version of the bulk dynamical model by Nicklow, Wakabayashi, and Smith (NWS).[4] The original NWS model calculation was based on a Born–von Karman model including axially symmetric interactions up to the third in-plane neighbors and first interplanar neighbors. Alldredge *et al.* added a second-neighbor interplanar interaction, whose effects will be discussed below. The NWS model, as well as the modified version by Alldredge *et al.*, unfortunately do not correctly reproduce the optical spectrum; in particular, the frequency of the optical A_{2u} mode at the Γ point is predicted to be about 42 THz by both versions of the model, whereas the experimental value[11] falls at 26 THz. Nevertheless, the modifications introduced by Alldredge *et al.* and the related observations they have made[12] retain all of their validity, and have relevant implications in surface dynamics, even in the framework of other more recent models. The important fact that Alldredge *et al.* pointed out is related to the interplanar coupling, and can be stated as follows: if the dynamical model does not include any (xy)-z coupling, i.e., a coupling between atomic motions parallel and perpendicular to the crystal layers, Rayleigh surface waves cannot be supported. In particular, this kind of coupling is completely neglected if the only interplanar interaction is the one between first nearest neighbors, i.e., between atoms which are aligned in the z direction. It is also important to note that neglecting second-neighbor interplanar interaction yields an inadvertent symmetry in the model, causing an additional degeneracy at the K point, as is the case for the models of Refs. 4, 7, and 9. Degeneracy splitting at the K point, however, could not yet be tested experimentally.

From the experimental point of view, careful inelastic helium-atomic scattering (HAS) studies of the lowest acoustic branch have been performed recently by Toennies and Vollmer.[13] The (001) surface dispersion relation for the Rayleigh wave ($S1$ mode) appears to be nearly coincident with the lowest TA bulk band, as measured with neutron scattering.[4] For the highest part of the spectrum, i.e., for the optical branches, the experimental

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situation is not so well established. In fact, the phonon spectrum of graphite extends up to about 50 THz for the optical branches polarized along the basal plane; at these energies, the neutron cross section is very small, causing a lack of experimental data on the bulk dispersion relations in this high-frequency section of the spectrum. The only direct experimental investigation of dispersion curves of graphite away from the Γ point at energies above 25 THz have been performed by means of reflection electron-energy-loss spectroscopy (REELS), which is a surface-sensitive technique. However, measurements by Wilkes, Palmer, and Willis,[14] and by C. Oshima *et al.*[15] show very good agreement with the available bulk data in the lower region of the spectrum.

The agreement of the recent REELS data with the predictions of the existing models[7,8] is not very good in the region above 15 THz: experimental points generally lie below the calculated curves for the lowest branches which correspond to in-plane polarization, and above the predicted values for the z-polarized branches. Moreover, the behavior of the highest $SP_{\parallel}$ and SH optical modes at the M point is clearly not correctly reproduced by the force-constant models, which predict a crossing, along the ΓM direction, between the SH optical branch and the $SP_{\parallel}$ acoustical one. Experimental data[15] show instead the presence of a gap, about 4 THz wide, between the optical SH and the acoustical $SP_{\parallel}$ modes at the M point. The BCM calculation, which includes the effects of the electronic response, does correctly reproduce this gap.

In the following sections, we present the modified version of the BCM for sp^2-bonded systems, with results for bulk graphite (Sec. II). We then show a calculation for a graphite slab with comparison to experimental data and to calculations with force-constant models (Sec. III). Finally, we discuss the transferability to other sp^2-bonded carbon structures (Sec. IV).

II. BULK LATTICE DYNAMICS OF GRAPHITE

The adiabatic bond charge model was developed by Weber in 1977 for the case of the tetrahedral sp^3 covalent bond,[16] and has provided results in very good agreement with the experimental data for silicon, germanium, α-tin, diamond, and III-V compounds.[17,18] The BCM is based on a representation of the valence-electron charge density by means of massless point charges [bond charges (BC)], which carry their own degrees of freedom and are dynamically coupled to the atomic displacements. For homopolar covalent crystals, the valence charge density has strong maxima along the bonds, and the BC's are located midway between neighboring atoms. The main idea in the BCM is that bond charges can mimic the adiabatic response of the electronic charge density to the atomic motion: in this sense, this is actually the simplest model containing the basic physics of the electron-phonon interaction. An immediate advantage of the BCM with respect to ordinary force-field approaches is given by the small number of parameters which are involved in the model, each of them having a clear-cut physical meaning, and proving to be easily transferable to different structures or geometries of the same material. The interactions included in the model are in fact all short ranged (first neighbors), except the Coulomb one, which is attenuated by the dielectric constant ϵ, and accounts for all the longer-range effects. Moreover, the numerical effort required to perform a BCM calculation is relatively modest, which allows for the study of very complex systems: recently, the model has been successfully applied to open and reconstructed semiconductor surfaces,[1,19] to a hydrogen-covered silicon surface,[20,21] to semiconductor superlattices,[22] and to the study of vibrational properties of hollow carbon clusters (fullerenes),[3,23,24] where the sp^2 coordination is also present. In the case of a tetrahedrally coordinated solid, the original BCM included, besides the Coulomb interaction, an ion-ion and an ion-BC nearest-neighbors central interaction, plus an angular BC-ion-BC interaction of the Keating type (which will be described below). The first problem arising in the translation of the BCM from the diamondlike structure into the graphite sp^2-bonded structure is that the model cannot describe automatically the interplanar bonding, which is actually of the Van der Waals type. In fact, we have found that the Coulomb interaction itself makes too small a contribution to the interplanar part of the dynamical matrix, because the electrostatic potential, generated by a periodic, planar array of positive and negative charges spaced about 0.7 Å, is nearly vanishing, together with its derivatives, at the graphite interplanar distance. For this reason, it is necessary to introduce two additional short-range force constants between the first and second *interplanar* neighbors.

Thus the interactions included in the model (see Fig. 1) are the following.

(i) The Coulomb interaction screened by the dielectric constant ϵ, between BC's and C atoms, which carry a charge $-ze$ and $+\frac{3}{2}ze$, respectively, according to the neutrality condition. This interaction acts between all particles, and is controlled by the model parameter z^2/ϵ.

(ii) A central two-body potential ϕ acting between neighboring atoms, which gives the parameters $\phi'_{\text{ion-ion}}$ and $\phi''_{\text{ion-ion}}$ its first- and second-order derivative, respectively. Note that $\phi'_{\text{ion-ion}}$ is not a disposable parameter, because it is determined as a function of z^2/ϵ by the

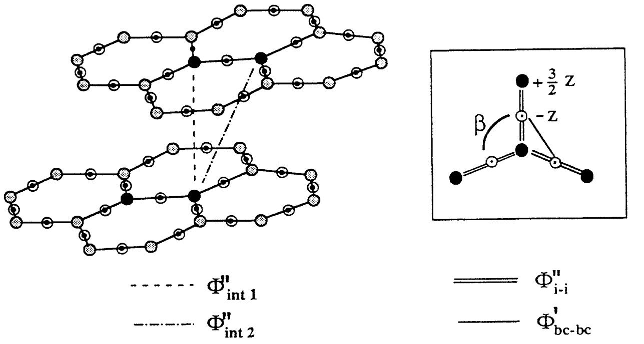

FIG. 1. The graphite structure, with bond charges located midway along the covalent bonds. The interactions considered in the present model are indicated. Highlighted are the atoms and BC's in the unit cell.

zero-stress condition, i.e., the condition that the derivative of the total energy with respect to the lattice spacing is zero. A numerical calculation, involving Ewald sums of first derivatives of the Coulomb potential, shows that this condition is satisfied when $\phi'_{\text{ion-ion}} = -3.629 e^2 z^2 / \tau_0^2 \epsilon$, where τ_0 is the nearest-neighbor distance.

(iii) An angular potential of the Keating form, involving the BC-atom-BC angle, controlled by the β parameter. The Keating potential has the form

$$V_k = -(\beta / 8\Delta)(\mathbf{d}_{oi} \cdot \mathbf{d}_{oj} - \Delta)^2 , \tag{1}$$

where $\mathbf{d}_{oi} = \mathbf{d}^0_{oi} + \mathbf{x}_{oi}$ is the vector joining the atom o to the BC i, $\mathbf{x}_{oi}$ is its displacement from the equilibrium value $\mathbf{d}^0_{oi}$, and $\Delta = -\frac{1}{3} |d^0_{oi}| |d^0_{oi}|$.

(iv) A central two-body potential ϕ_{int} acting between interplanar first and second neighbors, giving the parameters $\phi''_{\text{int},1}$ and $\phi''_{\text{int},2}$. Since the sum of the interplanar Coulomb interaction gives a negligible net force in the c-axis direction, the first derivatives of ϕ_{int} are both set equal to 0, in order to keep the equilibrium conditions fulfilled with the minimum number of free model parameters.

This produces a model which requires only five parameters. The two interplanar force constants, which are about two orders of magnitude smaller than the in-plane ones, can be determined in the rigid-layer approximation from just the experimental C_{33} and C_{44} elastic constants. The system formed by atoms and BC's has, as a whole, 30 degrees of freedom in the unit cell, and is treated in the harmonic approximation, which yields a 30×30 dynamical matrix.

Due to the vanishing mass attributed to the bond charges, the electronic degrees of freedom are eliminated through the adiabatic condition. The resulting effective dynamical matrix is then reduced to 12×12 and takes the form

$$\mathbf{D}_{\text{eff}} = \left\{ \mathbf{R} + \frac{z_{at}^2}{\epsilon} \mathbf{C}_R - \left[\mathbf{T} + \frac{z_{at} z_{bc}}{\epsilon} \mathbf{C}_T \right] \right.$$
$$\left. \times \left[\mathbf{S} + \frac{z_{bc}^2}{\epsilon} \mathbf{C}_S \right]^{-1} \left[\mathbf{T}^\dagger + \frac{z_{at} z_{bc}}{\epsilon} \mathbf{C}_T^\dagger \right] \right] \right\} , \tag{2}$$

where $\mathbf{R}$, $\mathbf{T}$, $\mathbf{S}$, $\mathbf{C}_R$, $\mathbf{C}_T$, and $\mathbf{C}_S$ are matrices representing, respectively, the short-range and Coulomb parts of atom-atom, atom-BC, and BC-BC interactions.

The interplanar coupling, represented by the two parameters determined by the experimental elastic constants, is found to have a substantial effect mainly on the two lowest phonon-dispersion curves along the Γ-A direction, and on the splitting between the lowest TA and TO branches along Γ-M and Γ-K. The three parameters z^2/ϵ, β, and $\phi''_{\text{ion-ion}}$ were fitted to the experimental phonon frequencies at the Γ point and along the Γ-M and Γ-K directions in the Brillouin zone.

The resulting best-fit parameter set and the corresponding calculated phonon dispersions are reported in the first row of Table I and in the upper part of Fig. 2, respectively.

The global agreement with the experimental data is good, except for the z-polarized modes, where our five-parameter model exhibits a behavior which is very similar to that predicted by the MH model,[7] and underestimates the lowest M-point frequency by about 40%. This fact can be explained by observing that, while passing from the tetrahedral three-dimensional structure to a two-dimensional one, the β (angular) parameter is no longer effective for displacement patterns along the z axis: when the C atoms move perpendicularly to the plane, an-

TABLE I. Model parameters for the five- and six-parameter versions of the bond charge model for bulk graphite. All force constants are given in units 10^4 dyn cm^{-1}, while Z^2/ϵ is adimensional.

Z^2/ϵ	β	$\Phi''_{\text{ion-ion}}$	$\Phi''_{\text{int},1}$	$\Phi''_{\text{int},2}$	$\Phi'_{\text{BC-BC}}$
1.31	32.80	136.1	−0.1273	0.091 31	0.0
1.31	32.80	136.1	−0.1273	0.091 31	8.397

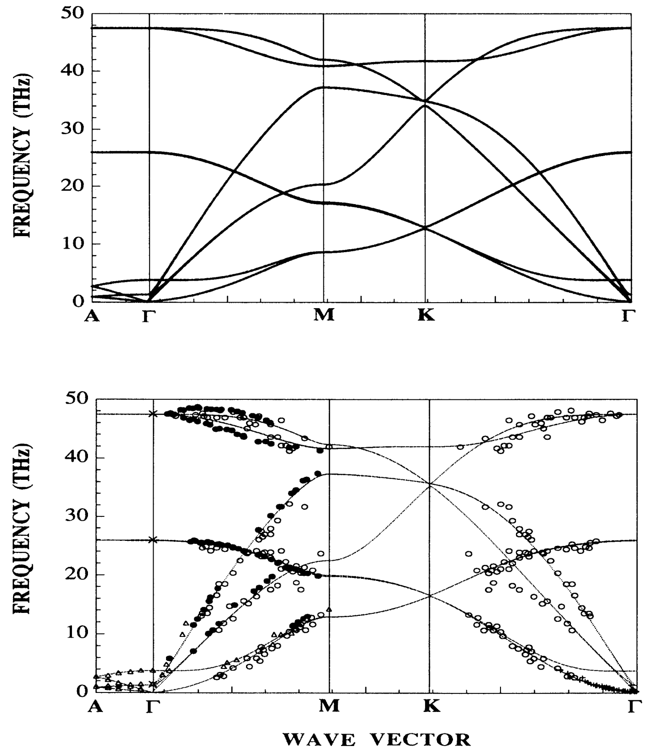

FIG. 2. Top: Five-parameter BCM calculated bulk dispersion curves for graphite: the behavior for the lowest branches is very similar to the one from the MH model (Ref. 7). Bottom: Calculated bulk dispersion curves from the six-parameter BCM, vs experiments: REELS data are by Wilkes, Palmer, and Willis (Ref. 14) (open circles) and by Oshima *et al.* (Ref. 15) (full dots). Also neutron data (Refs. 5 and 4) (open triangles) and atom scattering data (Ref. 25) (small crosses) are included. Stars show the frequencies at the Γ point. The REELS data by Wilkes, Palmer, and Willis are also plotted along $\overline{\Gamma}$-$\overline{K}$, since they are taken on a sample with random azimuthal orientation.

gles are not affected to first order. Neither can the second derivatives of the nearest-neighbor in-plane potential have an effect on this kind of atomic motion. For this reason, considering also that the interplanar coupling has only a small effect, the phonon-dispersion curves corresponding to out-of-plane atomic displacements depend in practice on the parameter Z^2/ϵ only.

The agreement with the experimental data can be greatly improved with the introduction of a minor modification to the original model: the addition of a BC-BC central interaction, producing a stiffening of the BC sublattice with respect to the z-direction motion. This stiffening could be interpreted as an effect due to the presence of the p_z orbitals, which are not accounted for in the above BCM description of the covalent sp^2 bond. The central BC-BC interaction, as the ion-ion one, enters the model by the first and second derivatives of a central potential. The second derivative has no effect on motion along the z direction, so we set it to 0 and retain only the $\phi'_{\text{BC-BC}}$ parameter. This raises to six the total number of parameters included in the model (see the second row of Table I). Also, this BC-BC interaction, having a nonzero first derivative, must be included in the vanishing-stress condition. It was found that the best results are obtained when $\phi'_{\text{BC-BC}}$ is balanced independently from the previously considered interactions, i.e., without influencing the z^2/ϵ and the $\phi'_{\text{ion-ion}}$ parameters. We simply balanced $\phi'_{\text{BC-BC}}$, which is positive, with a negative $\phi'_{(2)\text{BC-BC}}$ acting between next-nearest-neighbor BC's along the bond directions: $\phi'_{(2)\text{BC-BC}}$ must be taken equal to $-\frac{1}{2}\phi'_{\text{BC-BC}}$ in order to satisfy the vanishing stress condition. The value of $\phi'_{\text{BC-BC}}/d_{\text{BC-BC}}$ has been determined by fitting the frequency of the lowest mode at the M point. Its value is comparable with the effective BC-BC tangential force constant which arises from a linear term in the Keating potential, introduced by Weber for the diamond case,[16] but which is not required in our model.

In the lower part of Fig. 2, we show the comparison of the six-parameter calculation with experiments. The additional interaction has an important effect mainly on the TA and TO modes at the M point (see Table II).

TABLE II. Calculated vs experimental graphite phonon frequencies (cm^{-1}).

	Present calculation[a]	Observed[b]	Ref. 7	Ref. 8
$\omega(E_{2g_2})$	1582(1582)	1582	1575	1582
$\omega(E_{1u})$	1583(1583)	1587	1574	1587
$\omega(A_{2u})$	867(867)	868	850	867
$\omega(E_{2g_1})$	43(43)	42	44	42
$\omega(B_{1g_1})$	126(126)	127	127	127
ω_{TA} (M point)	466(286)	$\simeq$465	$\simeq$290	465
ω_{TO} (M point)	467(287)	$\simeq$480	$\simeq$300	478

[a] In parentheses, the values obtained without the central BC-BC interaction (first row of Table I).
[b] From Ref. 8.

Since the measurements of Wilkes, Palmer, and Willis[14] are taken on highly oriented pyrolytic graphite (HOPG) samples, which present random azimuthal orientation, their experimental points actually collect contributions from all the directions lying on the $z=0$ plane of the Brillouin zone (BZ). However, this is not a serious problem because of the fairly good acoustic isotropy of the system in the layer plane. To compare with the calculated curves, experimental data by Wilkes, Palmer, and Willis are then plotted also along the $\bar{\Gamma}$-$\bar{K}$ direction.

It is important to note that, due to the long-range Coulomb interactions and to the two short-range interplanar interactions which are considered, the BCM is not affected by the shortcomings and the inadvertent symmetries of the simple models, which were mentioned in Sec. I, and Rayleigh waves will be found in the slab calculation (Sec. III).

III. DYNAMICS OF GRAPHITE (001) SURFACE

Due to the very weak dispersion along the z direction, the (001) surface-projected bulk bands of graphite are very narrow and closely reflect the behavior of the bulk dispersion curves, except for the lowest acoustical region, where the two bulk branches corresponding to in-phase and antiphase motions of adjacent graphite planes become the upper and lower edges of the projected band.

When a (001) surface is created, only the weak interplanar bonding is broken, whereas the strong covalent sp^2 bonds between in-plane neighbors are preserved. For this reason, it is also expected that true surface branches will be very close to the edges of the projected bulk bands. This behavior was already reported in the slab calculation by De Rouffignac, Alldredge, and de Wette,[10] and has been recently confirmed by experiment[25] as well as in our work. As a matter of fact, in the slab calculation of Ref. 10, surface branches appear to be peeled off from the respective bulk bands by a frequency shift which is of the order of 0.02%. The nonzero but still small coupling between z and xy motions causes the ellipse of the sagittal plane polarized waves to be very elongated, allowing an easy distinction between quasilongitudinal and quasitransversal SP branches.

Since no surface calculation was available for the most recent bulk dynamical models, such as the MH or the AJD ones, we performed a slab calculation for these two models, employing a 21-layer slab. The results are shown in Fig. 3.

If BCM is employed instead of the MH or AJD model, the surface dynamics are again very similar to the projected bulk one. Again, the dispersion in the z direction is very small, and surface modes are nearly indistinguishable from the lower edges of the bulk bands. To determine whether or not a slab mode is a surface mode, one has to look at the behavior of the vibrational amplitudes $|\xi(m)|^2$ of the atoms as a function of the layer index m, from the surface layer toward the center of the slab. Of course, for the reasons explained above, the MH model gives no Rayleigh wave, whereas the AJD and the BCM do.

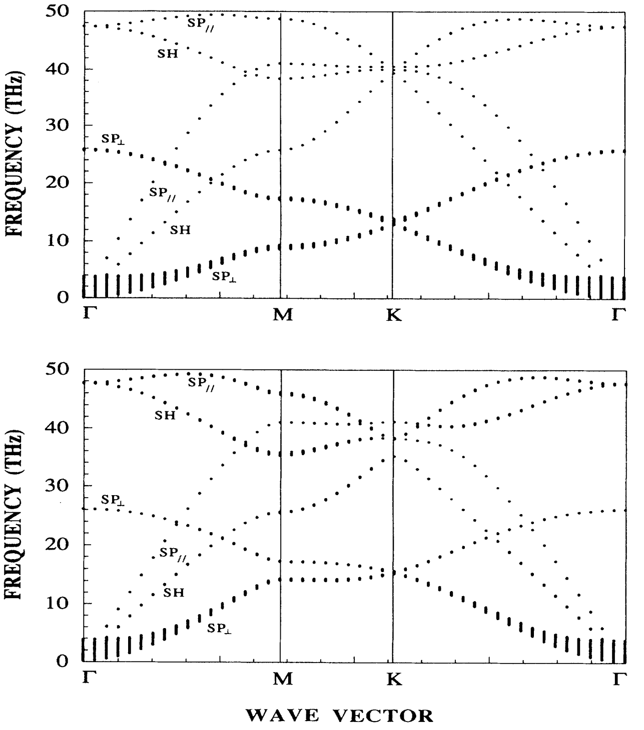

FIG. 3. The slab calculation (21 planes) for the MH (top) and AJD (bottom) models, along the $\bar{\Gamma}$-$\bar{M}$-$\bar{K}$-$\bar{\Gamma}$ directions.

IV. TRANSFERABILITY OF THE BCM PARAMETRIZATION TO DIFFERENT sp^2-BONDED CARBON STRUCTURES

The present parametrization of the dynamics of graphite includes, for what concerns the dynamics of a single layer, only three parameters (z^2/ϵ, β, and $\phi''_{\text{ion-ion}}$ in Table I) in its simplest version, and four (same table, with $\phi'_{\text{BC-BC}}$) in the version also including first- and second-neighbor BC-BC central interactions.

In particular, we can compare the case of our three-parameter calculation with the model described in Ref. 7. Both the calculations underestimate the frequency of the lowest acoustical phonon at the M point, but the highest part of the spectrum is more closely reproduced by the BCM. The case of our calculation including central BC-BC interactions can instead be compared with the calculation described in Ref. 8, as well as with recent single-layer calculations by Aizawa *et al.*[26] Again, the lowest part of the spectrum is reproduced in a similar way, but the BCM results for the highest optical branches are better.

The simplicity of the three-parameter BCM for the dynamics of a carbon layer makes its adaptation to different structures of two-dimensional carbon very easy. In fact, the transferability of parameters has been verified for the simpler version of the model, by the positive results obtained for the C_{60} (Ref. 3) and C_{70} (Ref. 24) fullerenes.

The application to C_{70}, in which there are eight nonequivalent classes of C-C bonds, has also raised the possibility of deducing an analytic form for the central repulsive ion-ion potential. In particular, it has been shown that, in a first approximation, one can assume that the bond charge is the same on all the bonds, and the effects of the charge transfer are recast into the ion-ion short-range potential. This approach can be refined if the bond charge is supposed to depend on the bond length. In both cases, the better parametrization for the repulsive ion-ion potential is found to be an exponential law.[24]

V. SUMMARY AND CONCLUSIONS

We have shown that the bond charge model is suitable to parametrize the dynamics of graphite. Six parameters at most are required to reproduce the experimental phonon frequencies and elastic constants of bulk graphite with a precision comparable to that of more involved force-constant models. The transferability properties of the minimal set of parameters (three) that are required to reproduce the dynamics of a single carbon layer were discussed, in connection with recent calculations on fullerenes. The satisfactory results obtained for C_{60} and C_{70}, together with the simplicity of this approach, suggest that this BCM should be suitable for predicting the vibrational spectra of complex sp^2 carbon architectures such as, e.g., giant fullerenes or other complex structures.[27]

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