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Bond-charge-model calculation of vibrational properties in small carbon aggregates: From spherical clusters to linear chains

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The bond-charge model, originally devised to calculate the phonon spectrum of bulk semiconductors and extended with success to describe the vibrations of graphite and fullerenes C_{60} and C_{70}, is applied to calculate the normal modes of vibration of small carbon aggregates, as the smallest fullerene (C_{20}), and odd-numbered linear and cyclic C_n clusters ($n=5-19$). The resulting spectra provide a satisfactory account of the experimental findings and are in overall agreement with the results of *ab initio* calculations.
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I. INTRODUCTION

The physics of small carbon clusters has become a well-established subject of research, gathering the interest of scientists from many different fields.[1] The existence of pure carbon clusters ranging from very small (5–10 atoms), to intermediate (20–100 atoms) and to large (hundreds of atoms) sizes, has been experimentally demonstrated.[2–9] Small clusters ($n \leqslant 20$), which have low-dimensional geometries (linear chains or rings, curved graphitic sheets, etc.) have been shown to play an important role in pyrolysis and combustion processes[10] as well as in astrophysical problems (linear C_5 has been detected in the IRC+10216 carbon star[11]). Polycyclic and cagelike clusters, including those belonging to the fullerene family, are believed to become energetically favored for more than 20–30 atoms.[12–14] Finally, to the family of C_n clusters also belong the large structures, like single or multilayer nanotubes and giant fullerenes, containing several hundreds of atoms.

Fullerenes and other carbon clusters, besides their intrinsic interest, display many potential applications as the building blocks of carbon-assembled materials.[15] Structural, electronic, and vibrational properties of the carbon aggregates have been extensively studied, using many different theoretical approaches, both *ab initio*[1,14,16–26] and semiempirical,[13,27–30] depending on the cluster size. Large structures are in general beyond the capabilities of present day *ab initio* methods, the limiting size being about ten atoms for the quantum-chemical configuration interaction (CI) method, and about one hundred atoms for calculations based on density-functional theory (DFT). Vibrational properties studies, in particular, require large computational efforts to be carried out within the framework of a fully *ab initio* scheme.[17,18,31] Theoretical predictions of the normal modes of vibration, however, can be extremely useful for the identification of the different C_n species and for the interpretation of their measured vibrational spectra.[9]

All that considered, a reliable, computationally simple semiempirical model such as the bond-charge model (BCM) remains a good option for the calculation of the phonon properties of carbon systems. BCM has been successfully applied in the past to bulk semiconductors,[32,33] open and reconstructed semiconductor surfaces,[34] and to GaAs superlattices.[35] More recently, some of us have developed the extension of BCM to sp^2 structures, such as graphite[36] and fullerenes C_{60} (Ref. 37) and C_{70}.[38] In the case of bulk graphite, our BCM employs five parameters (two of them being introduced to mimic the interplanar Van der Waals interaction). When used to compute the phonon dispersion curves, it yields an agreement with the experimental data which is equivalent to that obtainable using a 21-parameters force-constants model.[39] The observed eigenfrequencies of the 14 Raman and infrared (IR) active modes of fullerene C_{60} are reproduced by the (three-parameter) BCM calculation within 3%.[37] BCM has also been extended to solid C_{60} crystal[40] and to the calculation of IR and Raman spectra of C_{70}, yielding results of similar quality.[38] In the present paper, BCM is applied to fullerene C_{20} (dodecahedral cage), and then, with minor modifications, to *sp*-bonded structures, such as linear chains and planar rings. We show that in all cases the model is able to provide an overall account of the experimental findings, at a computational cost similar to that of force-constant models. With respect to the latter models, BCM requires fewer parameters (three in the case of fullerenes, reducing to two in the case of *sp*-bonded structures), all of them with a clear physical meaning. In particular, due account is given to the effects of the valence charge redistribution during the atomic motion.

The paper is organized as follows: first, we recall the features of the BCM. We then present the BCM results for the case of the dodecahedral C_{20} fullerene, for which the calculation is a straightforward extension of the work previously presented for C_{60} and C_{70}. In the following section, the extension of BCM to one-dimensional (*sp*-bonded) structures is presented. The results for the family of odd-numbered linear chains C_5-C_{19} and planar rings $C_{11}-C_{19}$ are given. For the linear chains, BCM results are compared with those obtained from a traditional force-constants model (FCM), where the electronic degrees of freedom are completely neglected. It is found that the FCM predicts a behavior for the highest vibrational frequency as a function of the chain length that is at odds with the experimental (and BCM) results. In the case of C_5, detailed results for the isotopic effects are also presented, in comparison with experimental data. Results for the 20 atoms polyacetylenic ring are also included, for the sake of comparison with the case of the icosahedral C_{20} cage.

II. MODEL

The adiabatic bond-charge model is based on a representation of the valence electron charge density by means of massless point charges, located near the maxima of the charge distribution, and free to follow adiabatically the ionic motion.[32] The bond charges (BC's) are meant to represent the first term of a multipole expansion of the valence charge distribution.

An immediate advantage of BCM, with respect to ordinary force-field models for the calculation of vibrational properties, is the small number of parameters required by the model. Moreover, the parameters have a clear physical meaning, and prove to be easily transferable among the different carbon structures. This can be understood in keeping with the fact that the BCM includes only first-neighbor phenomenological interactions, while long-range effects are taken into account through a screened Coulomb interaction.

In more detail, the interactions included in the model are the following. (i) The screened Coulomb interaction between negative BC and Carbon atoms, with the latter carrying a positive charge determined by the neutrality condition. This interaction acts among all particles, and is controlled by the model parameter z^2/ϵ. (ii) A two-body repulsive potential Φ acting between nearest-neighboring atoms, and parametrized by its first ($\Phi'_{\text{ion-ion}}$) and second ($\Phi''_{\text{ion-ion}}$) derivatives, respectively. (iii) For sp^3 and sp^2-bonded systems, an angular potential of the Keating form,

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

where $\vec{\mathbf{d}}_{oi}=\vec{\mathbf{d}}^0_{oi}+\vec{\mathbf{x}}_{oi}$ is the vector joining the atom o to the BC i, $\vec{\mathbf{x}}_{oi}$ is the variation with respect to the equilibrium value $\vec{\mathbf{d}}^0_{oi}$, and $\Delta=\vec{\mathbf{d}}^0_{oi}\cdot\vec{\mathbf{d}}^0_{oj}$ is proportional to the BC angle. Thus, V_K is controlled by the parameter β. Because the three-body Keating potential is built with scalar products, the condition of rotational invariance is automatically satisfied.

Since the Keating term for transverse angle-bending displacement vanishes at angles of 180 degrees, we find that this term can be neglected for *sp*-bonded linear systems.[41]

Note that $\Phi'_{\text{ion-ion}}$ is not a free parameter, because the equilibrium condition determines it as a function of z^2/ϵ and the atomic geometry.

In the harmonic regime, the elements of the BCM force constant matrix are obtained by analytical calculation of first- and second-order derivatives of the above potential. Using the matrix notation, the coupled dynamical equations for the ion and BC displacement vectors ($\mathbf{u}$ and $\mathbf{v}$, respectively) can be written as

$$\mathbf{M}\omega^2\mathbf{u}=\left(\mathbf{R}+\frac{z_{at}^2}{\epsilon}\mathbf{C}_R\right)\mathbf{u}+\left(\mathbf{T}+\frac{z_{at}z_{bc}}{\epsilon}\mathbf{C}_T\right)\mathbf{v}, \tag{2}$$

$$\mathbf{m}\omega^2\mathbf{v}=\left(\mathbf{T}^\dagger+\frac{z_{at}z_{bc}}{\epsilon}\mathbf{C}_T^\dagger\right)\mathbf{u}+\left(\mathbf{S}+\frac{z_{bc}^2}{\epsilon}\mathbf{C}_S\right)\mathbf{v}, \tag{3}$$

where $\mathbf{M}$ and $\mathbf{m}$ are the ion and BC mass matrices, ω is the eigenfrequency, and $\mathbf{R}$, $\mathbf{T}$, $\mathbf{S}$, $\mathbf{C}_R$, $\mathbf{C}_T$, and $\mathbf{C}_S$ are the short-range and Coulomb parts of atom-atom, atom-BC, and BC-BC interactions, respectively.

In the adiabatic approximation ($\mathbf{m}=0$), one solves Eq. (3) for $\mathbf{v}$ and replaces it into Eq. (2). This provides an equation for $\mathbf{u}$,

$$M\omega^2\mathbf{u}=D_{eff}\mathbf{u}, \tag{4}$$

where

$$\mathbf{D}_{eff}=\left[\mathbf{R}+\frac{z_{at}^2}{\epsilon}\mathbf{C}_R-\left(\mathbf{T}+\frac{z_{at}z_{bc}}{\epsilon}\mathbf{C}_T\right)\cdot\left(\mathbf{S}+\frac{z_{bc}^2}{\epsilon}\mathbf{C}_S\right)^{-1}\cdot\left(\mathbf{T}^\dagger+\frac{z_{at}z_{bc}}{\epsilon}\mathbf{C}_T^\dagger\right)\right] \tag{5}$$

is the effective ion-ion force-constant matrix, including the indirect ion-ion interaction mediated by the interposed BC.

The determination of the rest (equilibrium) positions of the BC's can be more or less demanding, depending on the degree of symmetry of the system. In the case of an infinite diamondlike crystal, or a graphite sheet, or an infinite linear chain, BC equilibrium positions are trivially found at the bond midpoints. In less symmetric cases, they must be determined by a separate analytic or numerical calculation. For example, in the case of a finite linear chain, the BC equilibrium positions are still on the bond axis, but displaced away from the bond center, especially in peripheral bonds. In ring and in spherical structures they are radially displaced, outwards with respect to the bond midpoints. Finally, in more complicated structures such as C_{60} and C_{70}, the equilibrium positions have been determined[37,38,42] by a numerical steepest descent relaxation algorithm. It must be stressed that the atomic positions, however, are never relaxed: they are an input data of the calculation. The global equilibrium condition is enforced, after having relaxed the BC positions, by computing the $\Phi'_{\text{ion-ion}}$ that make the given structure a stationary point of the total potential. A direct consequence of this approach, and of the choice of limiting the short-range interactions to first neighbors, is that not every low-symmetry atomic geometry can be stabilized. It would be of course possible to stabilize them at the price of an increase in the number of model parameters.

III. RESULTS

A. Cage C_{20}

The energetical ordering, and relative stability, of three different isomers of C_{20} (fullerenic dodecahedral cage, open bowl, and closed planar ring) is still a matter of debate. All these structures have a very similar total energy. Hartree-Fock (HF) calculations[18,23,25] predict the planar ring as the lowest-energy structure. DFT-LDA where LDA is local-density approximation (Refs. 18, 23, 43, and 44) and tight-binding[13,27] favor the cage structure. The inclusion of correlation effects in second-order Møller-Plesset perturbation theory (MP2) leads to different results favoring either the cage[18,25] or the bowl structure.[44] Coupled-cluster calculations favor, with almost the same energy, the bowl and the cage.[24] Calculations using the Becke-Lee-Yang-Parr (BLYP and B3LYP) hybrid method either predict a bowl or ring ground state.[21,44] On the other hand, the inclusion of gradient corrections on DFT or HF calculations produced large effects on the energetical ordering of the isomers, recovering the ring as the most stable configuration.[18,23,14] A diffusion Monte Carlo calculation[23] predicts the bowl as the lowest-energy structure. Moreover, a realistic calculation of the relative abundance of the isomers must also take into account the vibrational entropy contributions. The results of such a calculation indicate that the ring structure is the dominating one at the standard experimental conditions.[21]

The dodecahedral cage structure, which would make C_{20} the smallest fullerene, exists then probably only as a metastable state.[45] Calculations suggest also that this structure would undergo Jahn-Teller (JT) distortions, reducing the Y_h symmetry of the idealized regular dodecahedron.[18,21,25,27,43,46] Despite the lack of experimental data, many theoretical studies of the vibrational properties of cage C_{20} have been published in the past five years, both for the idealized[29] and for several JT distorted structures.[18,21,27,28]

TABLE I. Vibrational eigenfrequencies (cm^{-1}) of C_{20} in the Y_h cage structure, obtained with BCM. Degeneracies are 1, 3, 4, and 5, for *A*, *T*, *G*, and *H* modes, respectively. The bond length is set to 1.45 Å; the parameter values are $\Phi''_{\text{ion-ion}} = 144\times10^4$ dyn/cm, $\beta = 50.5\times10^4$ dyn/cm; $z^2/\epsilon = 1.63$.

A_g	T_{1u}	T_{2g}	T_{2u}	G_g	G_u	H_g	H_u
841	925	1065	990	970	682	525	736
			1195	1162	1313	1089	1464
						1510	

Note that the JT splittings in the vibrational spectra are generally limited, allowing for the recognition of multiplets of nearby frequencies, reminiscent of the original Y_h degeneracies of the symmetric structure.

Since the detailed geometry of the actual Jahn-Teller distorted structure is far from being established, and in the absence of any experimental data, the highly symmetric Y_h configuration has been chosen in the present work. This choice both simplifies the comparison with other calculations and allows us to establish a meaningful link to the normal modes of C_{60}, the paradigmatic fullerene. For example, it is easy to identify the (single) A_g totally symmetric mode that corresponds to the ''breathing mode'' of the molecule, at 841 cm^{-1}. In Table I we report the BCM results for the 14 different nonzero frequencies of the 54 normal modes of the molecule, together with their symmetry classification. These values were obtained with the same model parameters as in Ref. 37 and with $\Phi''_{\text{ion-ion}} = 144\times10^4$ dyn/cm, corresponding to a single bond length of 1.45 Å.[18,47] The geometrical relaxation of the positions of the BC's, performed as in Ref. 38, yields equilibrium positions that are radially displaced by 0.08 Å with respect to the bond centers.

The Raman active modes are predicted at 525, 841, 1089, and 1510 cm^{-1}, while the (single) IR line is found at 925 cm^{-1}. These values coincide within $\simeq 15\%$ with those obtained in Ref. 29 for the same structure, the agreement being better for the higher-frequency modes.[48] A comparison with the IR spectra predicted by recent, *ab initio* calculations for different Jahn-Teller distorted structures (and, eventually, with future experimental data) is also possible, taking into account that the modes generated from the splitting of our G_u, H_u, and T_{2u} modes will also become IR allowed. In the IR spectrum we expect, besides a triplet at about 925 cm^{-1}, additional multiplets at about 680, 740, 1000, 1200, 1300, and 1460 cm^{-1}. Such a distribution of the IR peaks agrees with the predictions of Ref. 21, with larger splittings ($\simeq 100\ \text{cm}^{-1}$) in the lower-frequency range, and smaller ones ($\simeq 10\ \text{cm}^{-1}$) for the higher frequencies.

B. Linear chains and planar rings

For clusters with less than 20 atoms, fullerenic structures with sp^2 coordination become energetically unfavored, in favor of structures with lower coordination number.[13,14] A general consensus exists about the ground-state geometry of C_5, C_7, and C_9: they are ''cumulenic'' linear chains, with

TABLE II. Calculated and observed vibrational frequencies for linear C_5 (cm^{-1}).

BCM[a,b]	BCM[a,c]	FC[a,d]	HF[e]	MP2[f]	B3LYP[g]	Expt.
2376	2164	2164	2344	2358 (2193)	2216	2164[b]
2043	1860	1840	2220	2018 (1877)	1969	
1507	1372	1337	1632	1471 (1368)	1440	
813	739	702	863	786 (731)	776	798±45[i]
567	509	508	648	487 (453)	533	512±45[i]
336	302	325	222	281 (261)	215	222±45[i]
141	127	132	112	130 (121)	116	101±45[i]

[a] Present work.

[b] BCM parameters, scaled from fullerene calculations: $\Phi''_{\text{ion-ion}} = 200\times 10^4$ dyn/cm, $\beta=0$, $z^2/\epsilon=1.63$. Bond length $r_0=1.3$ Å.

[c] BCM parameters: $\Phi''_{\text{ion-ion}}=163.7\times 10^4$ dyn/cm, $\beta=0$, $z^2/\epsilon=1.31$.

[d] FCM parameters: $K_{str}=91.56\times 10^4$ dyn/cm, $K_{bend}=2.29\times 10^4$ dyn/cm.

[e] Reference 17.

[f] Reference 31, in parentheses values scaled by a factor of 0.93.

[g] Reference 20.

[h] References 52 and 59.

[i] Reference 56.

interatomic distances of about 1.3 Å and very slight bond alternation (±0.02 Å). More generally, for $n<10$ theory predicts a different behavior for odd- and even-numbered C_n: the former are cumulenic linear chains, while the latter are planar monocyclic rings with a nearly isoenergetic linear isomer.[17,20,22,31] For $10<n<20$ a cyclic ground state is predicted for both odd- and even-numbered clusters, with polyacetylenic (partially dimerized) bonds for $n=12,16,20$ and cumulenic (undimerized) bonds in the other cases. From the experimental point of view, the situation is complicated by the fact that energetic differences between isomers are small.[14,23] Hence, clusters with geometries different from the ground-state one may be detected experimentally, due to entropic contributions. This is indeed the case for C_{13}, which has been observed as a linear chain.[50] Besides C_{13}, all chains belonging to the family of odd-numbered linear structures (C_5-C_{11}) have been experimentally identified with certainty. Cyclic structures, instead, seem to be more difficult to detect by spectroscopic techniques. When charged clusters are considered, the situation outlined above may change substantially: for example, linear chains from $C_5^- - C_{20}^-$ have been observed.[8,12] Finally, a solid carbon allotrope based on *sp*-hybridized C_n chains with 8–28 atoms stabilized by nonreacting terminal groups has been reported.[2,51]

Concerning vibrational properties, some of the IR active frequencies of odd-numbered linear C_n are experimentally known, both for clusters in the gas phase and deposited on inert matrices.[4,52–56] In some cases, the isotopic effects on the highest stretching mode also have been experimentally investigated.[31,52] Theoretical predictions, on the other hand, are available for the vibrational spectra of several clusters: C_2-C_{10} have been studied at the HF level;[17] electronic correlation effects have been considered for C_5 and C_7 using

TABLE III. Longitudinal frequencies for odd-numbered C_n linear chains up to 19 atoms (cm^{-1}). Experimental data are reported in parentheses, where available. BCM parameters as in column 2 of Table II.

$n=5$	$n=7$	$n=9$	$n=11$	$n=13$	$n=15$	$n=17$	$n=19$
2164 (2164,[a] 2169[b])	2160 (2128,[a] 2138[c])	2150	2142	2135	2129	2125	2121
1860	2014 (1893[d])	2065(1997[d])	2086	2096	2100	2102	2103
1372	1764	1918	1990	2028	2050	2064	2073
739 (798±45[e])	1424	1711	1853	1931	1978	2008	2029
	1006	1450	1678	1806 (1809[f])	1885	1937	1972
	523 (548±90[e])	1141 (1258±50[e])	1466	1654	1771	1848	1901
		788	1221	1476	1637	1744	1818
		404 (484±48[e])	946	1274	1483	1624	1722
			646	1050	1311	1489	1613
			329	806	1122	1339	1493
				547	918	1176	1361
				277	701	1001	1218
					474	815	1065
					239	620	903
						418	732
						210	556
							373
							188

[a] IR in matrix, Refs. 52 and 59.

[b] Gas phase, Refs. 4 and 53.

[c] Gas phase, Ref. 54.

[d] Reference 59 as reassigned in Ref. 31.

[e] Photoelectron spectroscopy, Ref. 56.

[f] Reference 50.

TABLE IV. Transversal frequencies for odd-numbered C_n linear chains up to 19 atoms (cm^{-1}). Experimental data are reported in parentheses, where available. BCM parameters as in Table III.

$n=5$	$n=7$	$n=9$	$n=11$	$n=13$	$n=15$	$n=17$	$n=19$
509 (512±45[a])	553 (496±110[a])	566	569	569	568	567	566
302 (222±45[a])	433	491	519	534	542	547	550
127 (101±45[a], 118[b])	292	394	451	484	504	517	526
	161	288	370	423	457	480	496
	65 (≃70[c])	186	285	355	402	435	459
		100	202	283	343	386	418
		40	128	214	282	334	374
			68	149	222	281	327
			27	93	165	228	280
				49	114	178	233
				19	71	131	188
					37	90	145
					14	55	106
						29	73
						11	45
							23
							9

[a] Photoelectron spectroscopy, Ref. 56.

[b] Gas phase, Ref. 53.

[c] Reference 60.

MP2 perturbation theory,[19,31] and within the Becke-Perdew (B3LYP) density-functional scheme for C_5-C_{13}.[20,22] Both the HF and MP2 calculated spectra must be scaled by a factor of about 0.9 in order to reproduce the experimental data.[57]

However, *ab initio* calculations become extremely heavy for more than 10 atoms. It is then clearly interesting to investigate the ability of a simple model to reproduce correctly the vibrational spectra of these molecules. In the following, we show that BCM is indeed an efficient tool for the study of C_n linear chains, being more precise that a trivial force-constants model, but also far from requiring the computational effort of an *ab initio* calculation, hence not suffering from their typical size limitations.

The interactions included in our BCM parametrization for sp-bonded carbon atoms are reduced, as previously mentioned, to the screened Coulomb interaction, plus a first-neighbor repulsion. Due to the lower coordination number and to the absence of sp^2 or sp^3 bonds, the three-body Keating potential can be dropped off. In this simple scheme, the model contains only two free parameters (the value of z^2/ϵ and that of $\Phi''_{\text{ion-ion}}$), $\Phi'_{\text{ion-ion}}$ being determined by the equilibrium condition. For simplicity, we have considered a unique bond length of 1.3 Å, neglecting the small differences (which are always less than 3%) that high-level calculations report for different bonds within the chains, and between different chains. However the bonds are not completely equivalent in our calculation, since the relaxed bond-charge positions are generally different for the different bonds. The small differences in the resulting frequencies obtained by taking also bond length differences into account cannot be considered very significant, due to the semiempirical character of the calculation. Once the angular potential is eliminated, the simplest approach of rescaling the parameter values used for fullerenes (where the Keating potential plays an important role) becomes less effective. However, we show the results obtained in this way for C_5 in column 1 of Table II. On the other hand, since reliable and precise experimental data are available for the highest vibrational mode of some well-characterized chain, namely, C_5 and C_7, the model parameters can be easily refitted. We have then simply fixed z^2/ϵ at the graphite value,[36] and fitted the (unique) value of $\Phi''_{\text{ion-ion}}$ in order to reproduce exactly the highest C_5 frequency. These parameter values have then been used to compute the full vibrational spectra of C_5 *and* of the other C_n chains, yielding very satisfactory results. The results for C_5 are reported in the second column of Table II. Those for the longer chains are shown in Tables III and IV.

In parallel, we have performed a force-constant (FC) model calculation with the same number of parameters (two), trying to fit them to the experimentally known data in a way similar to that of Ref. 52.

Even if, at a first sight, the main features of the spectra are almost equally well fitted in the FC and BCM approach, the advantages of the latter are evident. First of all, in the FCM the two model parameters (a stretching force constant K_{str} analogue to our $\Phi''_{\text{ion-ion}}$, and a bending force constant K_{bend}, corresponding to our factor $\Phi'_{\text{ion-ion}}/r_0$) determine, respectively and *independently*, the frequencies of the longitudinal and transverse modes. Since the experimental data on transverse frequencies are affected by large error bars, the bending force constant remains essentially undetermined. Moreover, in order to satisfy the equilibrium condition, it is necessary to consider short-range interactions extended at least to second neighbors, while in the BCM the only interaction acting beyond first neighbors is the screened Coulomb potential. In the BCM, stretching and bending frequencies

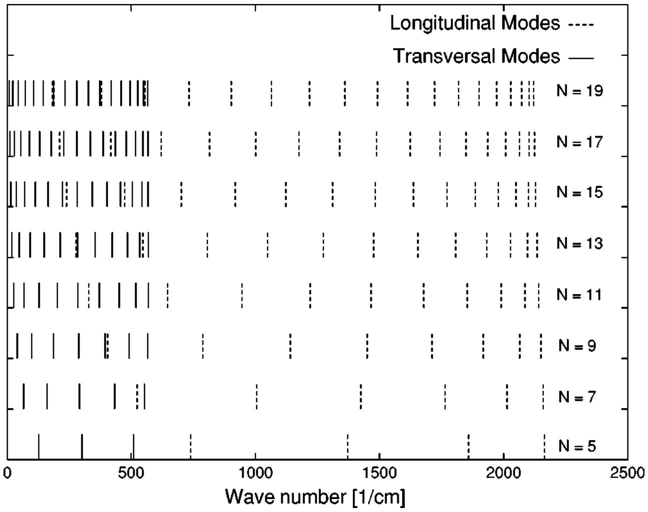

FIG. 1. Calculated eigenfrequencies for the set of C_n linear chains. Full lines, transversal modes; dashed lines, longitudinal modes.

cannot be varied independently: a natural interplay between them exists due to the consideration of the Coulomb interaction.

Another important difference between FC and BCM approaches is found in the different behavior of the highest vibrational frequency as a function of the number of atoms. In the BCM, the limiting value for $n \rightarrow \infty$ is approached from above, as shown in Fig. 1, where the vibrational spectra for the whole set of chains is reported, separating longitudinal (stretching) and transversal (bending) modes. In the FC model the highest frequency in the $n \rightarrow \infty$ limit, although similar to the BCM one, is approached from below. The experimental evidence supports the BCM predictions, at least for the shorter chains, where the highest frequency in C_5 is 20–30 cm^{-1} higher than in C_7.[52–54] Similar differences between the FCM and the BCM results are found in the behavior of the highest transversal frequency. Lowest and highest longitudinal and transversal frequencies, computed in both the FC and BCM approaches, are reported in Table V, for all of the chains considered.

The IR measurements on matrix-deposited C_5 performed by Vala and co-workers[52] allow resolution of the isotopic effects on the highest stretching frequency. In the BCM, as in the FC model, these effects can be computed in a straightforward way, within the defect-of-mass (DOM) approximation. We report in Table VI the results of such a calculation, in comparison with the experimental data. As was the case for the results of Ref. 52 (a FCM calculation), all the measured frequencies are reproduced within 3%, confirming the validity of the DOM approximation.

TABLE VI. Isotopic effect on the frequency of the highest longitudinal mode of linear C_5, compared with experiment (Ref. 52).

Isomer structure	Computed	Observed	Difference
12-12-12-12-12	2163.5	2164	−0.5
13-12-12-12-12	2160.8	2161	−0.2
13-12-12-12-13	2157.9	2158	−0.1
12-13-12-12-12	2143.7	2146	−2.3
12-12-12-13-13	2141.6	2144	−2.4
13-12-12-13-12	2140.3	2142	−1.7
13-13-12-12-13	2138.1	2140	−1.9
12-12-13-12-12	2129.6	2129	+0.6
13-12-13-12-12	2126.5	2128	−1.5
13-12-13-12-13	2123.2	2126	−2.8
12-13-12-13-12	2120.3	2122	−1.7
13-13-12-13-12	2117.6	2117.9	−0.3
13-13-12-13-13	2114.9	2117.5	−2.6
12-13-13-12-12	2109.4	2111	−1.6
13-13-13-12-12	2107.1	2109	−1.9
13-12-13-13-12	2105.4	2106.5	−1.1
13-13-13-12-13	2102.9	2104.5	−1.6
12-13-13-13-12	2084.9	2086	−1.1
13-13-13-13-12	2081.8	2083	−1.2
13-13-13-13-13	2078.7	2079.5	−0.8

Linear isomers of C_n with 11 or more atoms are predicted, by *ab initio* calculation, to be higher in energy than the corresponding cyclic structures. However, high-temperature preparation conditions, followed by a fast temperature decrease, allow the experimental detection of linear chains up to 13 atoms.[50] Despite the fact that no experimental data on cyclic C_n vibrational frequencies has been reported to date, it is clearly of interest to extend the BCM study to the ring isomers of $C_{11}-C_{19}$. Since in this case no experimental input can be used to fit the model parameters, the latter must be obtained by transferring or scaling those used for other structures. Similarly to the case of the linear chains, a single bond length of 1.3 Å has been considered for all the rings ($C_{11}-C_{19}$) within the full D_{nh} symmetry. This approximation (which, according to *ab initio* calculations of Ref. 22, is excellent for $C_{19}-C_{15}$ and becomes gradually less valid for smaller rings) simplifies the equilibrium condition (relaxation of the BC and determination of $\Phi'_{\text{ion-ion}}$), and allows one to keep the minimum number of model parameters (two). For our calculations, we have then simply used the

TABLE V. Highest longitudinal (L) and transversal (T) vibrational frequencies for C_n linear chains (cm^{-1}), computed with the present BCM and FCM (see text).

L	$n=5$	$n=7$	$n=9$	$n=11$	$n=13$	$n=15$	$n=17$	$n=19$
BCM	2164	2160	2150	2142	2135	2129	2125	2121
FCM	2164	2218	2240	2252	2258	2262	2265	2267
T	$n=5$	$n=7$	$n=9$	$n=11$	$n=13$	$n=15$	$n=17$	$n=19$
BCM	509	553	566	569	569	568	567	566
FCM	508	547	562	569	573	576	577	579

TABLE VII. Vibrational frequencies for odd-numbered C_n rings up to 19 atoms (cm^{-1}).

$n=11$	$n=13$	$n=15$	$n=17$	$n=19$
1977	2007	2026	2039	2048
1854	1914	1954	1982	2002
1605	1727	1809	1867	1908
1246	1447	1590	1693	1767
846	1094	1305	1462	1579
628[a]	728	971	1182	1347
546	547	638	870	1078
545	546	547	567	787
455	533[a]	546	547	547
448	481	497	546	545
305	478	496	508	515
287	367	463[a]	508	515
144	358	409	437	510
117	232	404	435	457
	215	297	409[a]	456
	105	287	344	380
	84	181	338	376
		167	242	366[a]
		80	233	291
		64	144	285
			132	200
			63	192
			50	117
				108
				50
				40

[a] Breathing mode.

values of z^2/ϵ and $\Phi''_{\text{ion-ion}}$ used for the linear chains. As for the other structures the bond-charge positions have been relaxed, and the $\Phi'_{\text{ion-ion}}$ determined by the equilibrium condition. The resulting frequencies, for the 11–19 atoms rings, are reported in Table VII. A comparison with Tables III and IV shows that going from the open (linear) to the closed (ring) topology yields, as expected, a reduction of the spectrum width, with larger effects on the smaller clusters. The width of the vibrational spectrum of the closed rings is hence intermediate between those of the fullerenic cage and of the open linear chains. In particular, the highest ring mode is lowered by 160–70 cm^{-1} with respect to the linear chain one, and the lowest ring mode is found at about 4.5 times the frequency of the lowest mode of the corresponding linear chain. In the case of linear C_5-C_{15} and ring $C_{11}-C_{15}$ our results can be compared with those of B3LYP calculations: BCM frequencies are generally slightly higher than the B3LYP ones, both for linear chains and planar rings.

C. Ring C_{20}

The successful application of BCM to planar odd-numbered rings suggests a further extension: the *sp*-bonded isomer of C_{20}, which is also a planar ring but, in contrast to the odd-numbered C_n clusters, has a polyacetylenic (i.e., partially dimerized) structure. This structure is predicted to be the most stable C_{20} isomer at both the HF and DFT generalized gradient approximation levels,[14,18,23,25] and, together with the ‘‘bowl’’ isomer, is likely to be present at the experimental conditions.[58] For our calculations we take bond distances of 1.24 Å and 1.35 Å, from Ref. 21. In order to facilitate the comparison of the results with those given in Table I, BCM calculations are reported for two different parameter sets: the ‘‘fullerene’’ set (rescaling the icosahedral C_{20} value of $\Phi''_{\text{ion-ion}}$ with the actual ring bond lengths), and the ‘‘linear chain’’ set used above for odd-numbered linear chains and cumulenic rings.

TABLE VIII. Vibrational modes for the polyacetylenic ring isomer of C_{20} as obtained in BCM. Bond lengths are 1.24 and 1.35 Å (Ref. 21). Results from other calculations are reported for comparison.

Degen.	LDA (Ref. 44)	HF (Ref. 18)	B3LYP (Ref. 21)	This work[a]	This work[b]
2	2189	2522	2240	(2260) 2255	2075
2	2177	2506	2231	(2204) 2186	2011
1	2111	2495	2143	(2278) 2277	2096
2	2076	2477	2119	(2106) 2073	1906
2	2025	2393	2101	(1965) 1918	1763
1	1994	2346	2078	(1843) 1787	1643
1	1589	1519	1563	(1636) 1584	1455
2	1450	1417	1440	(1464) 1411	1295
2	1175	1173	1174	(1180) 1131	1038
2	860	869	860	(864) 825	757
1	561	761	751	(662) 616	553
2	539–558[c]	757	731	(644) 600	539
2	531	702	640	(599) 599	538
2	503	618	566	(592) 554	497
2	493	615	547	(560) 553	496
2	484	577	493	(554) 533	489
2	480	544	492	(513) 484	434
1	474	536	468	(615) 615	552
2	440–471[c]	527	460	(484) 482	432
2	422	514	435	(416) 397	356
2	415	463	421	(397) 393	352
1	373	425	387	(404) 383	351
1	350	396	370	(320) 311	279
1	343	395	368	(311) 303	272
1	329	369	335	(300) 290	261
1	302	340	307	(290) 284	255
2	262	273	251	(206) 205	184
2	239	252	233	(205) 196	176
2	166	161	149	(119) 119	107
2	152	143	133	(114) 109	97
2	83–96[c]	69	64	(51) 51	46
2	56–73[c]	53	49	(42) 40	36

[a] BCM parameters, scaled from fullerene calculations: $\Phi''_{\text{ion-ion}}=230.2$ (short bond) and 178.5 (long bond) 10^4 dyn/cm, $\beta=0$ (in parentheses, results for $\beta=50.5\times10^4$ dyn/cm), $z^2/\epsilon=1.63$.

[b] BCM parameters, scaled from chains calculations: $\Phi''_{\text{ion-ion}}=183.8$ (short bond) and 147.1 (long bond) 10^4 dyn/cm, $\beta=0$, $z^2/\epsilon=1.31$.

[c] The LDA calculations of Ref. 44 are performed for a lower symmetry than that of the C_{10h} one.

The results of such calculation are shown in Table VIII.

The vibrational spectrum contains 32 frequencies (22 doubly degenerate and 10 nondegenerate modes), distributed from $\simeq 40$ to $\simeq 2200$ cm^{-1}. A comparison with the spectra computed by *ab initio* methods,[18,21,44] also reported in Table VIII, indicates overall agreement, with the linear chain parameters set to yielding frequencies that are systematically lower by about 10% with respect to those obtained using the fullerene parameters. The absence of modes in the region $\simeq 800 - \simeq 1100$ cm^{-1} (a ‘‘pseudogap’’ in the spectrum), predicted by BCM, is similarly present in HF, LDA, and B3LYP calculations. On the other hand, the width of a similar pseudogap around 1700 cm^{-1} shows a stronger dependence on the method of calculation employed. As pointed out in Ref. 21, a basic difference distinguishing the vibrational properties of the cage and the ring C_{20} is the presence, in the phonon spectrum, of low-frequency bending modes that are absent in the case of the cage (see Table I). In Ref. 21 it was found that the entropic contributions of these low-lying modes are responsible for a large relative abundance of the ring structure at the usual experimental conditions ($T \geqslant 1000$ K).

IV. SUMMARY AND CONCLUSIONS

We have shown that it is possible to compute the vibrational properties of a large class of pure carbon clusters—ranging from linear C_5 to fullerenes—using a reliable and computationally inexpensive method based on the bond-charge-model approach, obtaining an overall agreement with both experimental data and with *ab initio* results. The presented approach, due to the inclusion of the (classical) screened Coulomb interaction effects, is more efficient than traditional force-constant models with the same number of adjustable parameters. In particular, in the case of the linear chains, the BCM ensures that (a) a natural interplay between the frequencies of stretching and bending modes is present, (b) the experimental trend of the highest frequency with respect to the chain length is reproduced. Both of these features are missing in the case of the second-neighbors force-constant model. In conclusion, the BCM can be considered as an efficient tool for calculating the normal frequencies of carbon aggregates when *ab initio* calculations are not possible or available. Despite its simplicity, the presented model yields realistic theoretical eigenfrequencies that are quantitatively correct, for several clusters of very different size and dimensionality.

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