

Electron-phonon coupling for aromatic molecular crystals: Possible consequences for their superconductivity

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The electron-phonon coupling of a series of aromatic molecules is calculated on the same basis as for the alkali-doped fullerenes and graphite intercalation compounds. It is shown to be inversely proportional to the number of π bonded atoms, the effect of curvature being less important. The implication of these results for the superconductivity of the corresponding molecular crystals is discussed. [S0163-1829(98)07637-1]

A major step concerning the superconductivity of organic materials was the discovery, in 1991,¹ that the alkali-doped fullerenes (A_3C_{60}) have high critical temperatures: 33 K (Ref. 2) and even 40 K under pressure.³ Such values are completely different from what is obtained in graphite intercalation compounds (GIC) for which T_c is very low, the highest value being 5 K.⁴ This might seem surprising since, in both cases, the metallic states at the Fermi level originate from the π states on the carbon atoms. An explanation of this situation has been proposed on the basis of a conventional BCS mechanism with electron-phonon interaction.^{5,6} Although at its limits of validity this BCS mechanism now seems to be confirmed by numerous experimental data (for a review see Ref. 7). In this picture one basic difference between A_3C_{60} and GIC is induced by the curvature of the former.⁵ However this might not be the only physical quantity governing the strength of the electron-phonon coupling parameter λ . To clear up this important point we report, in this paper, on calculations of λ for a family of aromatic molecules, of which some are already known to give rise to molecular crystals. Our central result is that, although the curvature has some importance, the dominant parameter for fixing the magnitude of λ is the number N_π of atoms involved in the π states of the molecule, with the approximate law $\lambda \propto 1/N_\pi$. As we shall see this gives reasonable hope that some of the crystals built from such aromatic molecules may be superconducting with higher T_c than for A_3C_{60} .

In BCS theory the dimensionless electron-phonon coupling parameter λ is given by a general expression⁸ corresponding to a complex averaging over the Fermi surface. The molecular crystals we consider are characterized by weak interactions between the individual molecules, so that the band structure near the Fermi level corresponds to a set of narrow bands resulting from the broadening of the π states of each individual molecule. Under such circumstances it was shown for A_3C_{60} (Ref. 9) that λ can be factorized under the form

$$\lambda = N(E_F)V. \quad (1)$$

In this expression $N(E_F)$ is the density of states at the Fermi level (per molecule and per spin) which is completely determined by the strength of the *intermolecular* coupling between π states. On the other hand, V is a purely *intramo-*

lecular quantity, which measures the gain in energy due to the electron-phonon coupling, and is given by¹⁰

$$V = \sum_p \frac{1}{M\omega_p^2} \frac{1}{\nu^2} \sum_{i,j} \left(\frac{\partial h_{ij}}{\partial Q_p} \right)^2, \quad (2)$$

in which ν is the degeneracy of the partially filled molecular level which generates the conduction band at the Fermi level, $\partial h_{ij}/\partial Q_p$ is the electron-phonon matrix element between two of its basis states $|i\rangle$ and $|j\rangle$ for the molecular vibration mode Q_p of frequency ω_p normalized over the whole molecule. In the following we shall make use of Eqs. (1) and (2), assuming that their conditions of validity^{9,10} remain verified in the molecular systems we consider.

Let us concentrate first on the trends of V for the family of aromatic molecules listed in Table I with their number of atoms N_π involved in the π states of the molecule. Before discussing our numerical results let us first make use of a simple argument to have a guess for the dependence $V(N_\pi)$. For this we start from an Einstein approximation, i.e. replace ω_p^2 in Eq. (2) by an average value. We are then left with quantities $\sum_p (\partial h_{ij}/\partial Q_p)^2 = \sum_\alpha (\partial h_{ij}/\partial u_\alpha)^2$ where u_α are the components of the atomic displacements. In a Hückel or tight-binding (TB) model, where $|i\rangle$ and $|j\rangle$ are delocalized over the N_π atomic π states, each individual term $(\partial h_{ij}/\partial u_\alpha)^2$ is of order $1/N_\pi^2$ and their sum is then of order $1/N_\pi$. This proves that, at least in an average way $V(N_\pi) \propto 1/N_\pi$. This basic behavior can be confirmed analytically for a simple model of the C_nH_n molecules. This consists in a nearest-neighbors TB model for the electronic π states and a radial force constant model of strength K for the C-C bonds. Using the cyclic periodicity of the system one easily gets

$$V = \frac{2v^2}{Kn} \left(1 + \cos^2 \frac{2\pi p}{na} \right), \quad (3)$$

where p is an integer indexing the electronic state for which we calculate the coupling and v is the derivative with respect to the distance of the nearest-neighbor interaction. Obviously $N_\pi = n$ here so that the average of V over the states varies like $1/N_\pi$. The second term in Eq. (3) comes from the part of the diagonal contributions $i=j$ in Eq. (2) due to the symmetric vibrations which only shift the level.

We now discuss our numerical calculations performed on a family of aromatic molecules. This family can be subdivided

TABLE I. Intramolecular electron-phonon coupling V for a family of aromatic molecules. The electronic part has been calculated using two techniques whereas the phonon part has been performed in LDA. The molecular level on which the coupling is calculated can either be the lowest unoccupied molecular orbitals (L) or the highest occupied molecular orbitals (H) of the molecule. A screened value corresponds to a full value without diagonal contributions to the coupling. Convergence difficulties have occurred in the LDA coupling calculation for two molecules (C_{20} and C_{28}) which explains the absence of LDA values in the table.

Molecule	Molecular level (Degeneracy)	N_π	V (meV)	
			LDA Full/screened	TB Full/screened
C_5H_5	L (2)	5	368 / 367	350 / 330
C_6H_6	L (2)	6	380 / 291	302 / 251
C_7H_7	H (2)	7	326 / 320	265 / 258
C_8H_8	H (2)	8	200 / 188	163 / 163
Naphtalene	L (2)	10	221 / 170	190 / 159
Pyrene	L (1)	12	197 / 0	127 / 0
Anthracene	L (1)	14	166 / 0	117 / 0
Tetracene	L (1)	18	130 / 0	85 / 0
Coronene	L (2)	24	103 / 85	93 / 78
C_{60}	L (3)	60	52 / 47	49 / 44
C_{28}	H (3)	28		80 / 80
C_{20}	H (4)	20		183 / 183
Corannulene	L (2)	20	146 / 146	130 / 130
Pyridine	L (2)	6	368 / 306	301 / 254
Branch of IHIC	L (1)	10	251 / 0	217 / 0

vided into four groups. The first one contains unsaturated hydrocarbons like benzene, naphtalene, other polyacenes (anthracene, tetracene), coronene and pyrene. Monocyclic unsaturated hydrocarbon polyenes (i.e., all rings of the general formula C_nH_n) form a second group. Note that these two first groups have benzene in common. Another group contains molecules which belong to the fullerene family or which are similar to one of them: in particular we find here C_{60} , C_{20} , C_{28} , and corannulene, the top hydrogenated part of a C_{60} molecule. This forms the family of curved molecules. The last part contains molecules with an heteroatom, in particular related to the previous ones by the replacement of a CH group by a nitrogen atom. Such a substitution transforms benzene into pyridin. We also report results concerning a part of a pseudofullerene we have studied elsewhere¹⁰ which we call a branch also containing carbon and nitrogen atoms.

For each molecule, we have performed a geometry optimization using quantum-mechanical forces at the *ab initio* level in the local-density approximation.^{11,12} The electronic-structure calculation was then performed by two techniques. We have first used density-functional theory within the local-density approximation (LDA).¹³ We have also calculated the electronic structure with a nearest-neighbors empirical tight-binding (TB) method. The TB parameters have been extracted from Ref. 14 with a $d^{-2.8}$ dependence on distance for all hopping terms. Concerning nitrogen and hydrogen, we have used the same dependence on distance and the parameters have been fitted on LDA calculations of the electronic states of simpler molecules. We have then performed a calculation of the vibration modes in the same LDA formalism by determining the dynamical matrix and its eigenstates. For each vibrational mode calculated in this way, we have also employed a frozen-phonon model to establish the electron-phonon coupling matrix from which we get the parameter V .

The coupling is calculated using the two techniques, TB and LDA, by evaluating the new electronic structure in the distorted geometry. All numerical results are displayed in Table I. For each molecule, we make precise the molecular level used in the calculation and its degeneracy. We then give the intramolecular electron-phonon term V obtained using the two techniques (TB and LDA). The agreement between TB and LDA calculations is good as was already shown for C_{60} (Ref. 5) and IHIC.¹⁰ In both cases we display two sets of values, bare and screened (V_b, V_s). V_b is just the value obtained from a direct application of expression (2). When plotted in Fig. 1 versus N_π it exhibits a striking C/N_π behavior with $C \approx 1800$ meV, this dependence dominating a weaker curvature effect (as seen for the sequence

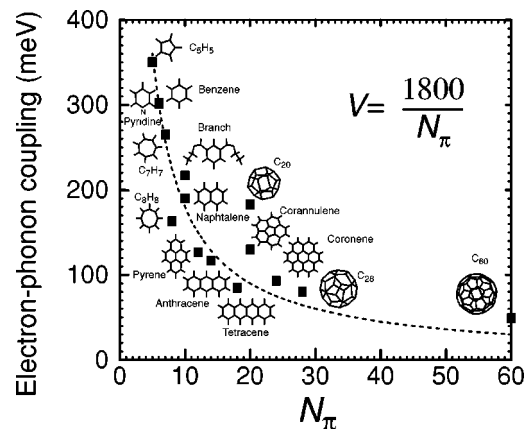


FIG. 1. π atom number dependence of the full electron-phonon coupling V given per molecule. These values have been obtained using a TB approximation for the electronic part and LDA for the vibrational one.

C_{60} , C_{28} , C_{20}). On the other hand, the screened value V_s is obtained by dropping from the matrix $\partial h_{ij}/\partial Q_s$ the diagonal terms corresponding to a simple shift of the level. As outlined in Ref. 5 this takes into account the fact that in the crystal, such a shift of one individual molecular level will be severely screened at least for the long-wavelength corresponding crystalline phonons. Thus the actual value of V to be used in calculations of λ is intermediate between these two extremes. As shown in Table I these are close for degenerate states but not for nondegenerate states for which $V_s=0$.

To discuss the implications of the previous results for superconductivity in the corresponding molecular crystals the best is to use McMillan's formula¹⁵

$$T_c = \frac{\hbar \omega_{\text{in}}}{1.2k_B} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right]. \quad (4)$$

In this expression ω_{in} is an average phonon frequency which does not vary much in our family of molecules, λ is the electron-phonon coupling constant defined before and μ^* is the Coulomb pseudopotential describing the electron-electron repulsion. We first analyze the trends in λ given by Eq. (1) as $N(E_F)V$. We can only get some rough estimate of $N(E_F)$ by realizing that the molecular crystals of interest will be characterized by weak "Van der Waals" interactions between molecules and thus by a similar broadening $\Delta \sim 0.3\text{--}0.5$ eV of the molecular states. The resulting average density of states is ν/Δ , lying between 2ν and 3ν [in $(\text{eV})^{-1}$]. This of course favors highly degenerate states but the application to the molecules of Table I shows that one could easily get high values of λ , e.g., of order 1.2 for benzene or even more if $N(E_F)$ corresponds to a peak value. Such strong-coupling values could also be realized for molecules of intermediate size (remember that for K_3C_{60} a value $N(E_F) = 14/\text{eV/spin}$ gives $\lambda = 0.7$ (Ref. 5)). Similar densities of states would lead to extremely large values of λ for the smaller molecules.

From these considerations alone one could then believe, with the same $\mu^* \sim 0.3$ (Refs. 7,16) as in A_3C_{60} compounds, that it is possible to get extremely large values of T_c . However such a conclusion obviously depends on the applicability of BCS theory to the corresponding molecular systems. In this regard, the main problem is caused by the relative im-

portance of correlation effects which is essentially measured by the value of the effective Coulomb repulsion U_{eff} between two electrons on the same molecule. A detailed discussion of this point is given in Ref. 7 for the A_3C_{60} compounds providing some justification of the use of BCS theory in that case. If we apply similar arguments to the present family of molecules a basic condition is obviously that the system must be metallic. An approximate condition for this to be realized is $U_{\text{eff}} \leq 2.5W$ where W is the bandwidth.⁷ This clearly does not favor small molecules like benzene for which U_{eff} is likely to be large. Even if this is not a definitive conclusion one might thus think that the situation for the molecules of intermediate size is more satisfactory in this regard with a reduction in U_{eff} . As regards the Coulomb pseudopotential μ^* the arguments derived in Ref. 7 show that in any case $\mu^* \leq 0.5$ leaving 0.4 as a reasonable value. This together with the larger values of λ for most of the molecules of Fig. 1 would ensure a substantial increase of T_c .

In conclusion we have calculated the electron-phonon coupling in a family of aromatic molecules. Our main result is that it varies mostly like the inverse of the number of atoms involved in the π states, while the dependence on curvature is weaker. This suggests that some of the corresponding molecular solids might lead to larger T_c than the A_3C_{60} compounds. Of course this at least requires that such molecular crystals can be synthesized and doped. The crystal data for most of the molecules we have examined here are known for a long time.¹⁷ Many reports deal with the reduction of different molecular species in solution¹⁸ which demonstrates the possibility of adding electrons from alkali atoms to the molecules. The major difficulty rests in the formation of a solid complex of reduced aromatic molecules which forms a doped crystal. This has already been shown for the polyacenes by Ubbelohde and co-workers.^{19,20} It has also been reported that the pseudofullerene IHIC, which has been studied elsewhere,¹⁰ could be reduced and crystallized. Furthermore, low-field microwave absorption results tend to indicate a superconducting transition near 50 K,²¹ which however has not yet been confirmed by susceptibility measurements, for reasons which are not yet clear at the moment. One can hope that an improvement of the doping sequence as well as of the degree of crystalline quality should lead to the synthesis of new superconductors with a high value of T_c .

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