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A Simple Predictive Model for Molecular Vibrations of Polycyclic Aromatic Hydrocarbons: An Extended Version of the MO/8 Model

Koichi Ohno, Risako Takahashi, Megumi Yamada, and Yumiko Isogai

Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba–ku, 980–8578 Sendai, Japan

A Simple Predictive Model for Molecular Vibrations of Polycyclic Aromatic Hydrocarbons: An Extended Version of the MO/8 Model[#]

Koichi Ohno,* Risako Takahashi, Megumi Yamada, and Yumiko Isogai

Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba–ku, 980–8578 Sendai, Japan

Abstract

Motivation. Polycyclic aromatic hydrocarbons (PAHs) are interesting targets of studies in connection with astrophysics of intersteller medium, molecular engineering of electronic devices, and environmental and biological chemistry of toxicity and carcinogenicity. Since topological connections between carbon atoms play decisive roles in properties of PAHs, we present a simple predictive model for molecular vibrations of PAHs with no additional information other than its topology, which can be applied to any size of PAHs without modification. The force field model is expressed in a quadratic form with valence internal coordinates. Conjugation effects of π electrons on the collective motions of electrons and nuclei in the carbon networks are included in the force constants for CC bond stretchings by using π electron bond–orders (BO) and bond–bond polarizabilities (BBP). This model previously developed as MO/8 is considerably improved as an extended version MO/8E to be used for both even and odd alternant PAHs and also for their excited states and ionic states.

Method. The MO/8E model is developed on the basis of Hückel and semiempirical molecular orbital methods.

Results. Ground–state molecular vibrations of PAHs can be predicted for both planar and out–of–plane modes for any size of PAHs with the accuracy of ca. 20 cm^{-1}. Excited–state vibrations can also be predicted in the accuracy of ca. 30 cm^{-1}. The computation time of the MO/8E model is much smaller (10^{-5}) than DFT and *ab initio* calculations.

Conclusions. The MO/8E model is efficient in predicting molecular vibrations of PAHs with 20 cm^{-1} (30 cm^{-1}) accuracy for ground (excited) states without any data except for topological connections of hexagonal rings.

Availability. MO/8 models will be released at the following address: http://qpcrkk.chem.tohoku.ac.jp.

Keywords. Molecular vibration; normal coordinate calculation; valence force field; polycyclic aromatic hydrocarbon; π electron conjugation effect; molecular orbital method.

Abbreviations and notations

PAH, polycyclic aromatic hydrocarbon	HMO, Hückel molecular orbital
BO, bond order	BBP, bond–bond polarizability
DFT, density functional theory	ΔP, bond order change
$\Delta\beta$, variation of the resonance integral	RMS, root–mean–square
SCFMO, self–consistent field molecular orbital	ex, excited–state
CI, configuration interaction	PPP, Pariser–Parr–Pople
CPU, central processing unit	CIS, configuration–interaction–singles

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* Correspondence author; phone: +81-22-217-6576; fax: +81-22-217-6580; E-mail: ohnok@qpcrkk.chem.tohoku.ac.jp.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are interesting and important systems in connections with astrophysics of intersteller medium [1,2], molecular engineering of electronic devices [3], and environmental and biological chemistry of toxicity and carcinogenicity [4] as well as physical [5] and organic [6] chemistry of aromatic compounds. Hexagonal networks of carbon atoms not only provide the geometrical frame–works of PAHs but also govern electronic and vibrational properties of PAHs. Electronic characteristics of π electron orbitals in PAHs can be well described by a simple molecular orbital theory such as the Hückel molecular orbital (HMO) theory, since electronic structures of PAHs are essentially determined by topological connections of CC bonds [7]. For molecular vibrations of PAHs, however, it has been a long history in the establishment of the counterpart simple theory based on topological characteristics. In the famous textbook for molecular vibrations by Wilson, Decius, and Cross [8], no simple force field model was presented for PAHs. In the famous textbook for molecular spectroscopy by Herzberg [9], an erroneous frequency of 1854 cm^{-1} for a ν_{14} b$_{2u}$ mode of benzene was listed based on a force field calculation, while the observed frequency is 1309 cm^{-1}, which is considerably lower than the calculation. It had been almost half a century since the Hückel theory was established for π electron orbitals, until simple valence force field models based on the HMO theory were proposed for molecular vibrations of PAHs by two independent groups almost coincidentally; Ohno's model was reported on August 2 in 1977 [10], and Cyvin's model was reported on October 25 in 1977 [11]. Ohno's model uses bond–order (BO) and bond–bond polarizability (BBP) for estimating diagonal and off–diagonal CC stretching force constants with pure hexagonal geometries, while Cyvin's model uses BO for estimating variations of both diagonal CC stretching force constants and CC bond lengths. Subsequent studies by Ohno [12–17] showed that the Ohno's model named MO/8 [17] (initially called as Method I/8 [10]) gave excellent average frequency errors of ca. 20 cm^{-1} for planar (in–plane) modes with no additional information other than topological connections of benzenoid rings. Ohno's MO/8 model was applied to various vibronic properties such as Franck–Condon factors, vibronically induced intensities, infrared intensities, Raman intensities, and vibrational frequency shifts on electronic excitation [12–21]. Although applications of Cyvin's model to planar vibrations for PAHs [22–27] gave average frequency errors of 50–100 cm^{-1}, much larger than those by Ohno's MO/8 model, Cyvin's model for out–of–plane vibrations [28–30] was found to be very satisfactory. These simple force field models for PAHs are worthy of further consideration because:

(1) It is conceptually important in chemistry to test how topology in chemical compounds plays important roles in their properties. For this purpose, PAHs are suitable systems, and force field models based on topological characteristics of PAHs provide good means and examples.

(2) It is practically important in many fields of chemical sciences to know vibrational frequencies and normal coordinates of molecules in sufficient accuracies. For this purpose,

sophisticated quantum chemical methods become available in recent years. Sophisticated calculations based on *ab initio* methods or density functional theory (DFT) are, however, so demanding in computation that their applications have been limited to relatively small systems in comparison with the ranges of semiempirical methods or very simple methods such as Ohno's and Cyvin's models. In our experience, Ohno's and Cyvin's methods are at least 10^5 times more efficient than *ab initio* and DFT methods. This in other words corresponds to a dramatic reduction of computation time *e.g.* from one year to only 5 min.

(3) There are increasing interests on considerable numbers of very large PAHs [31] and carbon networks of graphite fragments or graphenes [32, 33] and graphite [34,35] in connection with fullerenes and nanotubes [36]. For these very large systems, simple force field models are much more suitable than sophisticated quantum chemical methods.

In the present study, the MO/8 model developed by Ohno for planar vibrations of PAHs [10,17] and the Cyvin's model for out–of–plane vibrations of PAHs [28–30] were combined to produce an extended version of the MO/8 model (MO/8E) that can be used for both planar and out–of–plane vibrations. Since the original MO/8 program only deals with even numbers of π electrons, this limitation was removed so that the new version may be applied to ionic states of even alternant PAHs as well as neutral states of odd alternant PAHs. Excited–state normal mode calculations developed by Ohno and Takahashi [15,21] were also incorporated in the MO/8E program. By the use of this MO/8E program, molecular vibrations of PAHs can be predicted both for planar and out–of–plane modes in the ground electronic state of any size of benzenoid PAHs in the accuracy of ca. 20 cm^{-1}, and excited–state vibrations can also be predicted in the accuracy of ca. 30 cm^{-1}.

2 METHOD AND CALCULATIONS

The MO/8 model was designed in analogy with the HMO theory as a predictive means for all PAHs to the infinite size without any modification and extra knowledge except for topological connections of hexagonal rings [10,17]. The following general treatments were used throughout.

(1) Wilson's **GF** matrix method [8] is used for normal coordinate calculations.

(2) Potential functions are produced in terms of valence internal coordinates in the quadratic form. Some anharmonicity effects are, however, incorporated in the potential parameters, which are set so as to reproduce observed fundamental frequencies. As for CC stretching force constants, diagonal terms include the bond–length dependence via BO in order to take important parts of anharmonic contributions into account especially for the σ force constant depending crucially on the bond length [17].

(3) Geometrical structures of hexagonal networks are fixed to be pure hexagons with a CC distance of 1.397 Å, a CH distance of 1.084 Å, and a valence angle of 120˚. The dependence of CC

stretching force constant on the CC bond length is taken into account by using BO terms. The assumption of the fixed geometries on **G** matrix was estimated to lead frequency errors of 3–8 cm^{-1}, which is much smaller than the accuracy of the MO/8 model of ca. 20 cm^{-1}.

(4) Force field parameters are fixed at the standard values for all systems. The standard parameters for planar modes in the MO/8 model were very similar with the individually optimized parameters for naphthalene [17].

(5) Atomic masses are set as follows, ^{1}H = 1.007825, ^{2}H = 2.014102, ^{12}C = 12, ^{13}C = 13.003355.

(6) Local redundancies around carbon atoms are eliminated by setting up local symmetry coordinates in terms of orthonormal linear combinations of three angles about the carbon atoms. Other types of redundancies are eliminated by transforming the secular equation in a symmetric form by Miyazawa's method [37]. **G** is diagonalized as ^{t}**AGA** = **DD**, where **A** and its transpose ^{t}**A** is orthogonal matrix, and **D** is a diagonal matrix whose elements are square root of eigenvalues of **G**. The secular matrix then becomes a symmetric form as **H** = ^{t}**(AD)FAD** [38].

(7) Geometrical structures are generated automatically from topological connections of hexagonal rings, and numberings of atoms and bonds as well as definitions of internal coordinates are automatically made in a systematic way. No other input data are required except for a specification of isotope constitution. Numbering of atoms, Cartesian coordinates, and some other generated information are listed in the output data.

(8) Although the extension of the MO/8 model to excited–state vibrations require some additional parameters for introducing excited–state properties in the force field, these parameters taken from conventional semiempirical theories with no modifications [13,15,17,21] are also fixed for all PAHs.
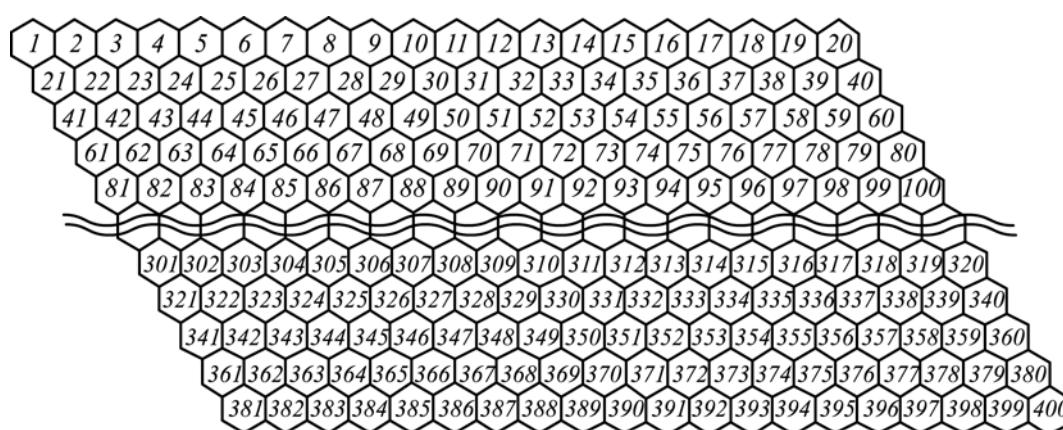

Figure 1. Honeycomb grids for rings input data. The hexagonal rings are numbered from the left top to the right bottom.

In the present study, the MO/8 model [10,17] previously established for planar vibrations of PAHs was extended to include the following functions in the computing program coded in Fortran,

and this new version of the program was named as the MO/8E model:

(1) The MO/8E program can be applied to normal coordinate calculations for out–of–plane vibrations as well as for planar vibrations.

(2) Since the original MO/8 program only deals with even numbers of π electrons, this limitation was removed so that the MO/8E program may be applied to odd π electron systems such as ionic states of even alternant PAHs as well as neutral states of odd alternant PAHs.

(3) Excited–state normal mode calculations developed by Ohno and Takahashi [15,21] were also incorporated in the MO/8E program.

(4) The MO/8E program uses a rings input convention based on honeycomb grids shown in Figure 1. For example, a rings input for anthracene $C_{14}H_{10}$ is *1 2 3* and a rings input for coronene $C_{24}H_{12}$ is *2 3 21 22 23 41 42*, etc. as listed in Table 1. Any part of the honeycomb grids can be used arbitrarily within the range of 400 rings in Figure 1. Much larger grids may be used optionally. The MO/8E program with a data of topological connections of hexagonal rings automatically performs normal coordinate calculations of the perhydro ^{12}C system in the neutral ground electronic state. With some optional input data, different isotope constituents, ionic states, excited states may also be treated. Specifications of additional input data can be used to control output data of normal mode analyses together with some information on electronic–state calculations such as HMO properties and π electron excited–state properties.

Table 1. Examples for rings input data

PAH	Rings Input Data										
Benzene	*1*										
Naphthalene	*1*	*2*									
Anthracene	*1*	*2*	*3*								
Phenanthrene	*2*	*21*	*41*								
Naphthacene	*1*	*2*	*3*	*4*							
Pyrene	*2*	*21*	*22*	*41*							
Triphenylene	*3*	*21*	*22*	*42*							
Chrysene	*1*	*2*	*22*	*23*							
Benzo[*a*]pyrene	*2*	*3*	*4*	*21*	*22*						
Pentacene	*1*	*2*	*3*	*4*	*5*						
Perylene	*2*	*3*	*22*	*41*	*42*						
Benzo[*g,h,i*]perylene	*2*	*3*	*21*	*22*	*41*	*42*					
Coronene	*2*	*3*	*21*	*22*	*23*	*41*	*42*				
Ovalene	*2*	*3*	*4*	*21*	*22*	*23*	*24*	*41*	*42*	*43*	
Tribenzo[*a,g,m*]coronene	*3*	*23*	*24*	*42*	*43*	*44*	*45*	*62*	*63*	*81*	
Kekulene	*3*	*4*	*5*	*22*	*25*	*41*	*45*	*61*	*64*	*81*	*82*	*83*
Phenalenyl radical	*2*	*21*	*22*								
Tribenzophenalenyl radical	*3*	*23*	*42*	*43*	*44*	*61*					

2.1 Force Field Model for Planar Modes

The force field for planar modes has been established as the MO/8 model [10,17]. Internal coordinates are classified into CC and CH stretchings, and CCC and CCH angle bendings. Highly

correlated motions of CC stretchings are described based on conjugated π electron theory by Coulson and Longuet–Higgins [39–42]; CC stretching force constants F_{ij} are expressed as follows:

$$F_{ii}(\text{CC}) = f_1 + f_2(P_i - P_0) + f_3(\Pi_{ii} - \Pi_0) \qquad \text{for } i = j \tag{1}$$

and

$$F_{ij}(\text{CC} - \text{CC}) = f_3\Pi_{ij} \qquad \text{for } i \neq j \tag{2}$$

Here, P_i is the bond–order (BO) for the CC bond i, and Π_{ij} is the bond–bond polarizability (BBP) for a couple of CC bonds i and j. P_0 and Π_0 are the BO and the diagonal BBP for benzene, respectively. BO and BBP are evaluated by HMO calculations. Potential parameters f_1, f_2, f_3 and others $f_4 = F(\text{CH})$, $f_5 = F(\text{CCC})$, $f_6 = F(\text{CCH})$, $f_7 = F(\text{CC–CCC})$, $f_8 = F(\text{CC–CCH})$ were determined as average values of individually optimized values for benzene, naphthalene, anthracene, pyrene, and triphenylene [10,15,17]: $f_1 = 6.821$, $f_2 = 5.450$, $f_3 = 3.646$, $f_4 = 5.072$, $f_5 = 0.928$, $f_6 = 0.504$, $f_7 = 0.430$, and $f_8 = 0.199$ in units of 10^2 Nm^{-1}, 10^{-18} Nmrad^{-2} or 10^{-8} Nrad^{-1}, as shown in Figure 2. The resonance energy β for HMO is set to -1. Some anharmonicity effects are considered via optimization to observed fundamental frequencies. It should be noted that in addition to the BBP terms for collective motions of CC bonds, varieties of diagonal CC stretching constants for various CC bond lengths, which is related to anharmonicity, are taken into account as the BO terms in Eq. (1).
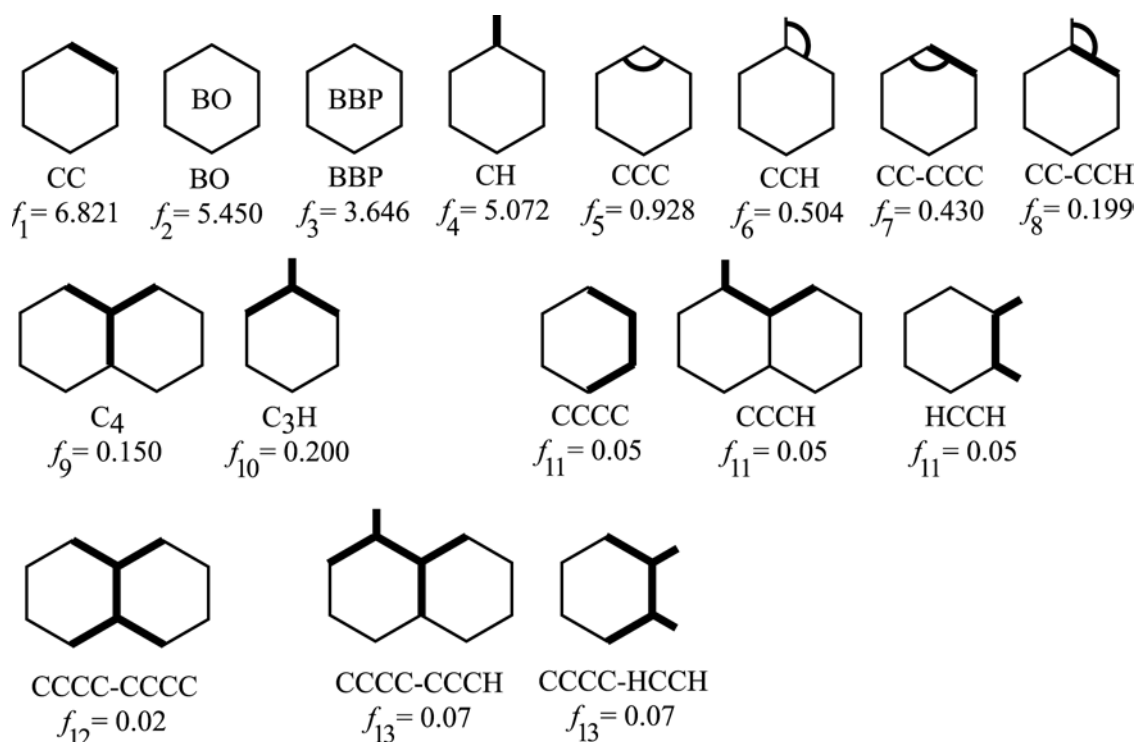

Figure 2. Force field parameters in the MO/8E model. f_1–f_8 are for planar modes, and f_9–f_{13} are for out–of–plane modes.
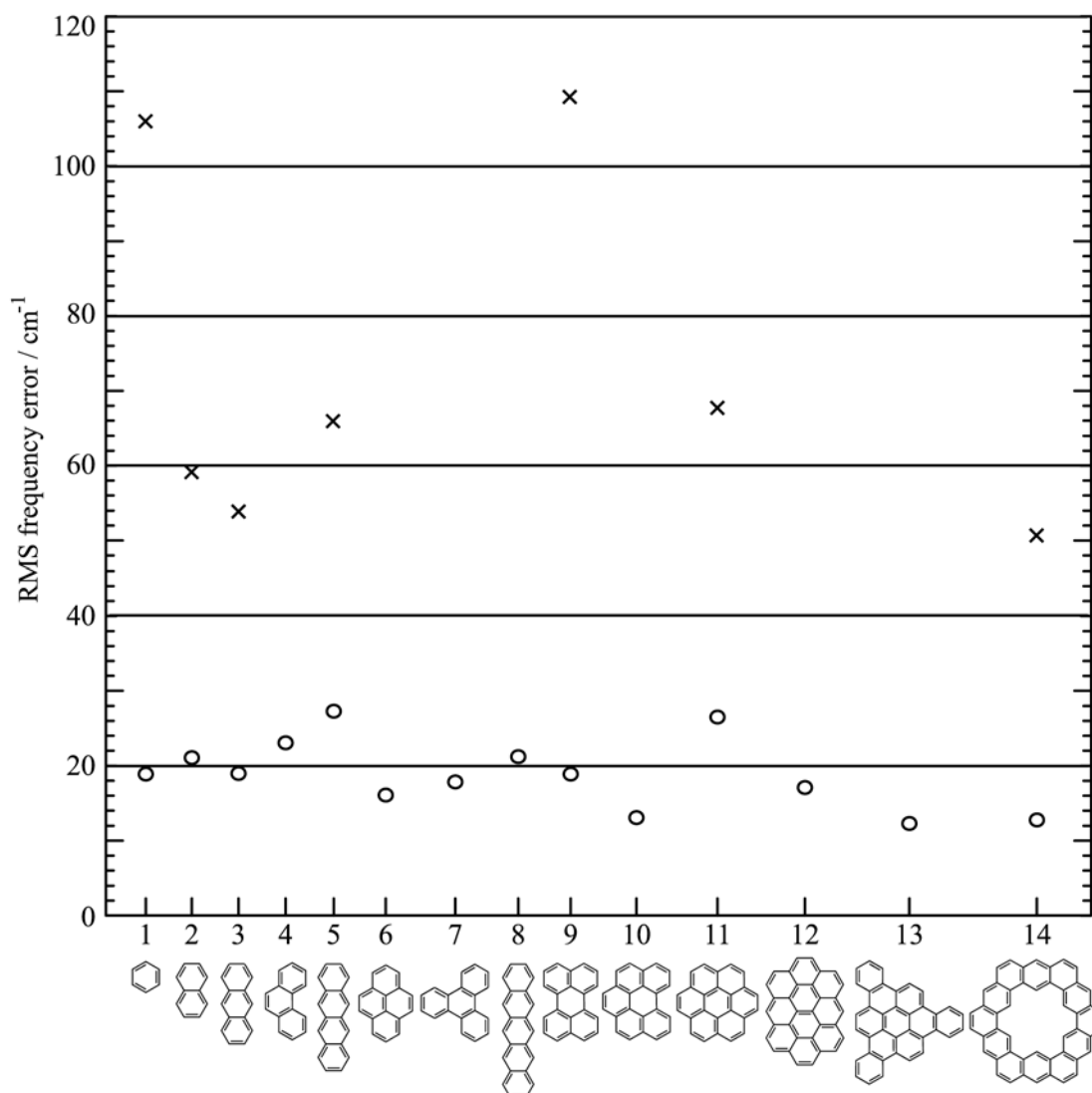
Figure 3. A comparison of RMS frequency errors for planar modes in the ground state. **1**. benzene C_6H_6 and C_6D_6; **2**. naphthalene $C_{10}H_8$ and $C_{10}D_8$; **3**. anthracene $C_{14}H_{10}$ and $C_{14}D_{10}$; **4**. phenanthrene $C_{14}H_{10}$ and $C_{14}D_{10}$; **5**. naphthacene $C_{18}H_{12}$; **6**. pyrene $C_{16}H_{10}$ and $C_{16}D_{10}$; **7**. triphenylene $C_{18}H_{12}$ and $C_{18}D_{12}$; **8**. pentacene $C_{22}H_{14}$; **9**. perylene $C_{20}H_{12}$; **10**. benzo[g,h,i]perylene $C_{22}H_{12}$; **11**. coronene $C_{24}H_{12}$; **12**. ovalene $C_{32}H_{14}$; **13**. tribenzo[a,g,m]coronene $C_{36}H_{24}$; **14**. kekulene $C_{48}H_{24}$. (×) Five parameter model for planar modes by Cyvin *et al*. [11,23–27]; (○) The MO/8 model with the standard parameter set by Ohno [15–20].

The MO/8 model with the above parameters gives excellent results with root–mean–square (RMS) frequency errors of ca. 20 cm^{-1} for the ground state of typical PAH [10,17]. Figure 3 compares RMS frequency errors of the MO/8 model and Cyvin's model for planar vibrations. It should be noted that experimental data used for comparison in Figure 3 contain all planar modes including CH stretching and available perdeutero data.

2.2 Bond–Bond Polarizability

According to the π electron theory developed by Coulson and Longuet–Higgins [39–42], the BBP in Eqs. (1) and (2) are defined as differentiation of BO with respect to the resonance integral:

$$\Pi_{ij} = \partial P_i / \partial \beta_j \tag{3}$$

where P_i is the BO for the i–th CC bond, β_j is the resonance integral for the j–th CC bond, and Π_{ij} is the BBP for a couple of the i–th and j–th CC bonds. It is of note that Eq. (3) requires a numerical evaluation of BO change ΔP associated with the variation of the resonance integral $\Delta\beta$, which should be evaluated from the difference between the HMO calculation with the standard β value ($\beta = -1$) and the additional HMO calculation with a slightly changed β value (*e.g.* $\beta = -1.0001$) for a respective CC bond. These additional HMO calculations should be made for all CC bonds in order to obtain all BBP matrix elements via Eq. (3).

The perturbation treatment by Coulson and Longuet–Higgins [39] leads to an alternative method to obtain BBP from the following equation:

$$\Pi_{ij} = 2\sum_{k}^{occ}\sum_{l}^{un}(C_{ka}C_{lb} + C_{kb}C_{la}) \times (C_{kc}C_{ld} + C_{kd}C_{lc})/(\varepsilon_k - \varepsilon_l) \tag{4}$$

where C_{ka} is the HMO coefficient for the k–th molecular orbital and the a–th atomic orbital, and ε_k is the orbital energy of the k–th molecular orbital. The bond indices i and j refer to atomic pairs of a–b and c–d, respectively. The summations for k and l should be taken for the occupied and unoccupied orbitals, respectively. Since BBP values can be evaluated via Eq. (4) from only one HMO calculation with the standard β value, this equation (4) has been used in the MO/8 model [10,17]. This treatment, however, limits the applicable range of the MO/8 model only for the systems having even numbers of π electrons. Otherwise, the denominator including the energy difference between occupied and unoccupied orbital energies in equation (4) becomes vanishing to lead to divergence.

In order to avoid divergence in equation (4), the MO/8E program automatically switches over to Eq. (3) when the number of π electrons is odd. Although the use of Eq. (3) is rather time–consuming in BBP calculations, this is not serious, because the computation time for BBP is almost negligible (a few percents) in comparison with the total computation time for normal coordinate calculations. Numerical values of BBP from Eqs. (3) and (4) using HMO were found to be identical within a very small discrepancy of 10^{-5}. Such a small discrepancy in BBP only leads to a negligibly small frequency difference of 10^{-4} cm^{-1}.

2.3 Force Field Model for Out–of–Plane Modes

The out–of–plane force field parameters f_9–f_{13} listed in the unit of 10^2 Nm^{-1} in Figure 2 were the same as those of Cyvin's model [28]. The out–of–plane motion around a carbon atom is classified into two types, C_4 and C_3H. The torsional motions are grouped into CCCC, CCCH, and HCCH.
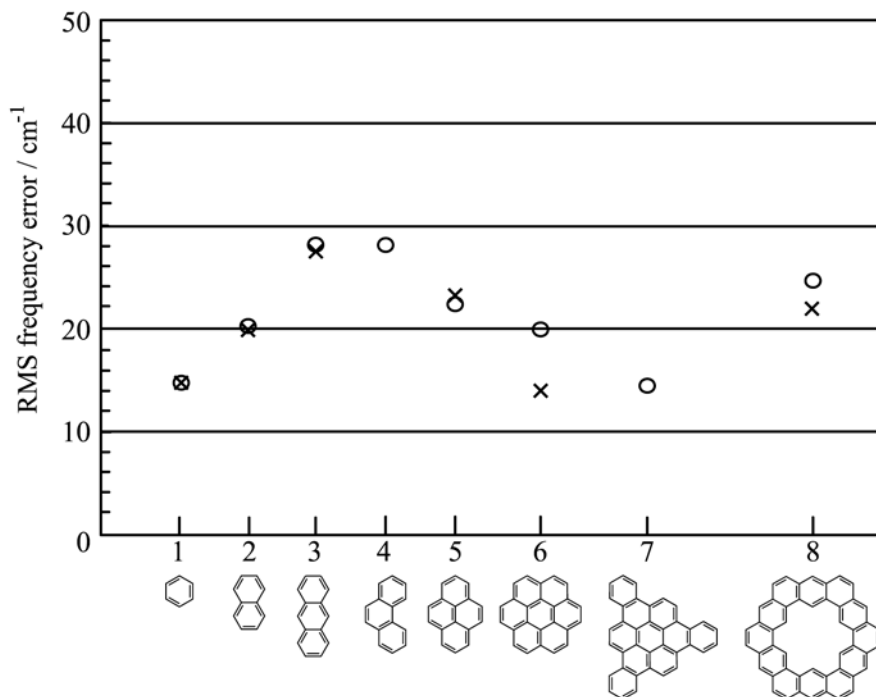
Figure 4. A comparison of RMS frequency errors for out–of–plane modes. **1**. benzene C_6H_6; **2**. naphthalene $C_{10}H_8$; **3**. anthracene $C_{14}H_{10}$; **4**. phenanthrene $C_{14}H_{10}$; **5**. pyrene $C_{16}H_{10}$; **6**. coronene $C_{24}H_{12}$; **7**. tribenzo[*a*,*g*,*m*]coronene $C_{36}H_{24}$; **8**. kekulene $C_{48}H_{24}$. (×) Five parameter model by Cyvin *et al*. [28–30] with the bond–order bond–length relationship; (○) The present MO/8E model with pure hexagonal geometries.

According to Cyvin's model, interaction constants are only retained for CCCC–CCCC, CCCC–CCCH, and CCCC–HCCH, and other types of off–diagonal terms are neglected. Although the force fields were the same as the Cyvin's model, computed frequencies of out–of–plane modes for naphthalene, anthracene, coronene, and kekulene showed an average difference of 5.6 cm^{-1} between the present and Cyvin's calculations. This is because the present model uses pure hexagonal structures, which are slightly different from those estimated via the bond–order–bond–length relationship in Cyvin's model [28]. As can be seen in Figure 4, RMS frequency errors with respect to observed fundamental frequencies were ca. 20 cm^{-1} for both Cyvin's and the present models. Calculated out–of–plane CH bending frequencies of *solo*, *duo*, and *trio*/*quartet* types have characteristic ranges of frequencies, as can be seen in Figure 5.

2.4 Force Fields for Ionic States

Important ionic states of PAHs are related to π electrons. Force fields for planar modes of PAH ions can be established by simple replacements of BO and BBP in Eqs. (1) and (2) by respective BO and BBP for ionic states. This treatment can also be extended to excited ionic states with a π electron excitation. Ionic–state BO can be obtained by simply removing (or adding) one electron from (or to) the respective molecular orbital.
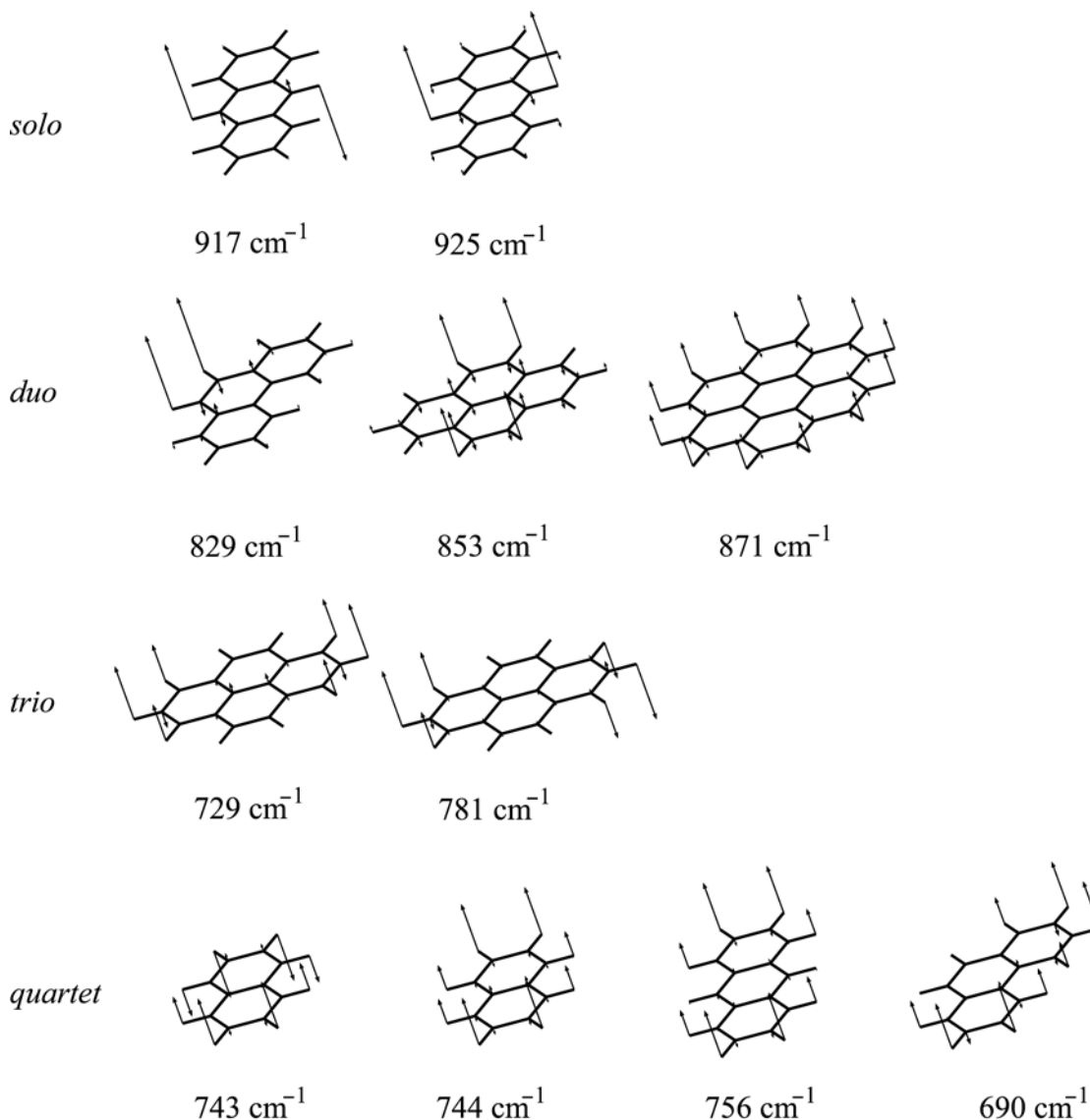
Figure 5. Out–of–plane CH bending modes of *solo*, *duo*, *trio*, and *quartet* types.

In principle, the procedure seems to be very easy. However, there are several problems in practical calculations:

(1) Since a chemically stable PAH contains an even number of π electrons, then its ion becomes an odd π electron system, for which Eq. (3) rather than Eq. (4) should be used in BBP calculations.

(2) In the case of high symmetry systems such as benzene and coronene, degenerate orbitals cause erroneous BO values depending on the choice of a moiety of the degenerate components. In such cases, the difficulty can be removed by setting an equal weight for the degenerate components in BO calculations.

(3) In some cases HMO gives accidental degeneracy. A typical case is perylene which has four fold degeneracy at $\varepsilon = \alpha \pm \beta$ (α and β are Coulomb and resonance integrals, and ε is the orbital

energy). This problem of HMO method can be removed by using semiempirical self–consistent field molecular orbitals (SCFMO).
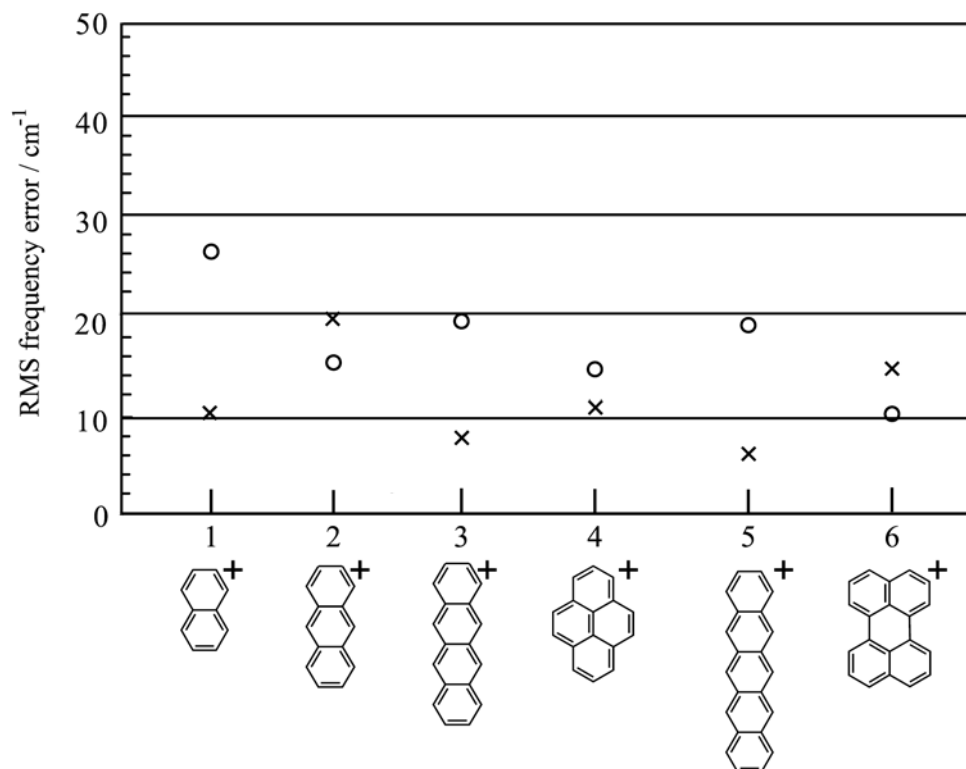

Figure 6. A comparison of RMS frequency errors in the ground state cation. **1**. naphthalene cation $C_{10}H_8^+$; **2**. anthracene cation $C_{14}H_{10}^+$; **3**. naphthacene cation $C_{18}H_{12}^+$; **4**. pyrene cation $C_{16}H_{10}^+$; **5**. pentacene cation $C_{22}H_{14}^+$; **10**. perylene cation $C_{20}H_{12}^+$. (○) The present MO/8E calculations with BO and BBP for ions. (×) DFT B3LYP/6–31G(d) calculations.

In the MO/8E program, the HMO treatment for BO and BBP is used for ionic state calculations, unless the SCFMO treatment is specified optionally. RMS frequency errors with respect to observed fundamental frequencies of the ground state for typical PAH cations were shown in Figure 6.

2.5 Force Fields for Excited Electronic States

Low lying excited electronic states of PAH originate from π–π* transitions. Force fields for π–π* states of PAHs can be given by simply replacing BO (P_i) and BBP (Π_{ij}) for the ground state in equations (1) and (2) by BO (P_i^{ex}) and BBP (Π_{ij}^{ex}) for respective excited states. Other parameters are set to be the same as the original MO/8 model. Such a simple extension of the MO/8 model was made to the lowest π–π* states of pyrene by Borisevich *et al*. [43], though they did not report the method to obtain the excited–state BO and BBP from HMO and the details of their normal coordinate calculations. Since π–π* states are not accurately described by HMO, configuration interaction (CI) calculations based on SCFMO are necessary. In a previous paper, Ohno and Takahashi [21] reported this technique using CI wave functions denoted as MO/8ΔΠ in detail and compared with an alternative simple method [15] denoted as MO/8Δ*E* which deduces excited–state

force fields from π–π* transition energies. In the present MO/8E model, excited–state force fields of MO/8ΔΠ were constructed with excited–state BO (P_i^{ex}) and BBP (Π_{ij}^{ex}) from CI wave functions obtained by semiempirical calculations.

Since the important excited states of PAHs are due to π–π* transitions, a semiempirical Pariser–Parr–Pople (PPP) method for SCFMO [44,45] is used. The overlap approximation of an exponential type is used for the resonance integral β with a proportionality constant yielding β = −2.38 eV at r(CC) = 1.397 Å and Z = 3.25 for the effective nuclear charge for the Slater–Zener atomic orbitals. The Nishimoto–Mataga approximation is used for the electron repulsion integrals [46], since this approximation yields satisfactory results for both excitation energies and oscillator strengths in good agreement with experimental electronic spectra. In the CI calculations, 36 configurations of single excitations from six occupied to six unoccupied orbitals (25 configurations for naphthalene) are taken. Excited–state BO P_i^{ex} are obtained with the SCFMO coefficients and CI coefficients. Excited–state BBP Π_{ij}^{ex} are obtained from P_i^{ex} via numerical evaluations of equation (3). The unit for Π^{ex} was renormalized to the case of β = −1, since this unit is used in the MO/8 model.

2.6 Additional Calculations

For comparison with the present MO/8E calculations, we performed some DFT calculations by Gaussian 94 [47]. In view of conventionally used levels, the DFT B3LYP/6–31G(d) level was chosen as a reference in the present study.

3 RESULTS AND DISCUSSION
3.1 Ground–State Planar Modes
3.1.1 Even numbers of π electron systems

As can be seen from Figure 3, RMS frequency errors for planar modes of various PAHs with even numbers of π electrons are ca. 20 cm^{-1} for the MO/8 model. This excellent propensity is retained in the present MO/8E model. Important remarks of the MO/8 force fields for planar vibrations are summarized as follows:

(1) Highly correlated effects of collective motions of CC bonds on remote CC bonds are included through off–diagonal BBP in equation (2). This is very important, since delocalization of π electrons transports effects of a particular part of distortion or perturbation to other parts in the π electron network via BBP. If off–diagonal CC stretching force constants for *meta*–positions are missing, an extraordinary high frequency is given for a v_{14} b_{2u} mode in benzene [48,15,17]. Lack of off–diagonal CC stretching force constants in Cyvin's model is responsible for the relatively high RMS errors for planar modes in Figure 3.

(2) It is well known that stretching force constants considerably change depending on the bond

lengths. Thus, the MO/8 treatment fixing the ring structure at a pure hexagon seems to yield considerable inaccuracies. However, effects of bond strengths on the force constants are almost directly included into the diagonal CC stretching force constants in the MO/8 force field via BO terms in equation (1). Distortion of geometrical structures from pure hexagons does not deteriorate qualities of the G matrix, which causes much smaller differences of 3–8 cm^{-1} in comparison with the RMS errors of 20 cm^{-1}. Pure hexagon treatments have an advantage to avoid considerable efforts or costs searching experimental structure data or performing geometry optimizations.

(3) Molecular vibrations usually contain strong anharmonicity. Vibrational frequencies obtained in harmonic approximation deviate from observed fundamental frequencies toward higher values. Thus, *ab initio* and DFT calculations by recent quantum chemistry packages require scale factors, which are sometimes troublesome, since they depend more or less on the employed method as well as choice of basis functions. The MO/8 model has been parametrized for some typical PAHs to reproduce observed fundamental frequencies. In this optimization process, anharmonicity effects were taken into account to a certain extent in the MO/8 force model. Furthermore, it should be noted that the diagonal CC force constants parametrized as a function of BO in Eq. (1) include important parts of anharmonicity in relation to the σ force constant depending considerably on the bond length.

Table 2. Planar frequencies of phenalenyl radical $C_{13}H_9$ (cm^{-1}).

	DFT [a]	MO/8E [b]		DFT [a]	MO/8E [b]
a_1'	3109	3057	e'	3106	3057
	3085	3056		3093	3055
	1518	1512		3082	3054
	1393	1398		1557	1566
	1087	1080		1545	1546
	765	755		1418	1408
	608	612		1323	1343
a_2'	3090	3054		1224	1252
	1468	1462		1176	1178
	1384	1364		1098	1101
	1191	1187		1029	1040
	1143	1149		809	816
	567	609		466	478
				416	436

[a] DFT B3LYP/6–31G(d) calculation with a scale factor of 0.970 by this work
[b] This work

3.1.2 Odd numbers of π electron systems

No experimental data could be available for chemically unstable odd π electron systems. DFT B3LYP calculations for even alternant hydrocarbons of naphthalene, phenanthrene, and anthracene [49] yielded RMS errors of ca. 30 cm^{-1} without scaling and smaller errors of 10–20 cm^{-1} with scaling treatments. Such qualities of the DFT method may also be expected for odd π electron systems. Thus, we compared our MO/8E calculations for phenalenyl radical and tribenzophenalenyl

radical with DFT B3LYP/6–31G(d) calculations with a typical scale factor of 0.970.

Table 3. Planar frequencies of tribenzophenalenyl radical $C_{25}H_{15}$ (cm^{-1}).

	DFT [a]	MO/8E [b]		DFT [a]	MO/8E [b]
a'	3130	3057	e'	3129	3057
	3114	3056		3115	3056
	3109	3056		3108	3055
	3094	3055		3094	3055
	3083	3054		3083	3054
	1612	1606		1608	1599
	1565	1552		1560	1554
	1507	1512		1538	1544
	1454	1443		1489	1485
	1429	1425		1436	1437
	1372	1377		1374	1381
	1351	1347		1344	1350
	1310	1312		1302	1313
	1256	1233		1234	1255
	1184	1182		1218	1206
	1161	1158		1173	1172
	1114	1102		1150	1157
	1035	1030		1096	1094
	960	985		1036	1026
	881	875		908	921
	675	678		809	808
	633	657		660	680
	535	552		592	605
	377	392		525	557
	310	291		332	336
				171	153

[a] DFT B3LYP/6–31G(d) calculation with a scale factor of 0.970 by this work
[b] This work

Concerning with the CH stretching modes, calculated MO/8E frequencies are in a similar range as those for even π electron systems. DFT calculations with a scale factor of 0.970 have a propensity giving rather higher frequencies for CH modes. When all planar modes are compared, average frequency differences are 22.8 cm^{-1} for phenalenyl radical and 25.8 cm^{-1} for tribenzophenalenyl radical. When CH stretching modes are excluded, average differences considerably reduce to 14.8 cm^{-1} and 12.5 cm^{-1}, respectively. Since average differences without CH stretching are more reliable, we may conclude that planar frequencies for odd π electron systems by the MO/8E model are also in the RMS error range of ca. 20 cm^{-1}. Calculated vibrational frequencies for phenalenyl radical and tribenzophenalenyl radical are listed in Tables 2 and 3, respectively.

3.2 Ground–State Out–of–Plane Modes

Table 4 compares calculated and observed [50] out–of–plane frequencies of benzene. The present MO/8E results for benzene were found to be identical with those by Cyvin *et al*. [28]. The results were also compared with DFT calculations [51]. The RMS errors are very similar in the range of 13–14 cm^{-1}. Cyvin's (MO/8E) model yielded an error of -23 cm^{-1} for a_{2u} mode, whereas

DFT methods gave an error of -29 or -20 cm^{-1} for e_{2u} mode.

Table 4. Observed and calculated frequencies for out–of–plane vibrations of benzene (cm^{-1}).

	Obs. [a]	DFT [b]	DFT [c]	Cyvin [d]	MO/8E [e]
b_{2g}	990	979	997	985	985
	707	696	696	686	686
e_{1g}	846	836	833	831	831
a_{2u}	673	671	661	650	650
e_{2u}	967	938	947	968	968
	398	401	394	398	398
RMS error		14.1	13.0	14.3	14.3

[a] Observed frequencies taken from [50]
[b] DFT B3LYP/6–31G(d) frequencies taken from [51]
[c] DFT B3LYP/6–311++G(d,p) frequencies taken from [51]
[d] Calculated frequencies by Cyvin *et al*. taken from [28]
[e] This work

Table 5. Observed and calculated frequencies for out–of–plane vibrations of anthracene (cm^{-1}).

	Obs. [a]	DFT [b]	Cyvin [c]	MO/8E [d]
b_{1g}	956	975	956	954
	747	772	761	760
	477	486	444	442
	242	242	255	248
b_{2g}	975	996	981	982
	916	927	930	925
	896	902	869	868
	771	782	755	761
	577	586	572	562
	284	271	293	295
a_u	958	996	979	981
	858	847	874	873
	743	764	704	708
	552	534	505	499
	137	122	142	144
b_{3u}	952	969	969	966
	892	871	922	918
	732	743	758	767
	504	494	428	422
	383	394	396	392
	96	93	102	100
RMS error		16.4	26.8	27.6

[a] Observed frequencies taken from [52]
[b] DFT B3LYP/6–31+G(d) frequencies taken from [53]
[c] Calculated frequencies by Cyvin *et al*. taken from [29]
[d] This work

Table 5 compares calculated and observed [52] out–of–plane frequencies of anthracene. DFT frequencies [53] are also listed. Cyvin's [29] and the present results gave very similar frequencies, and the average difference was 4.6 cm^{-1}. This is satisfactory in view of our treatment using pure hexagons. Large disparities from observed and DFT frequencies are found for a few modes; observed 743 cm^{-1} (a_u), 552 cm^{-1} (a_u), and 504 cm^{-1} (b_{3u}) are much higher than those by Cyvin and

MO/8E. In this regard, Cyvin's out–of–plane force fields may be improved.

Table 6. Observed and calculated frequencies for out–of–plane vibrations of pyrene (cm^{-1}).

	Obs.[a]	Cyvin[a]	MO/8E[b]
b$_{1g}$		932	926
	842	837	837
		497	493
	221	272	276
b$_{2g}$		986	989
	970	960	963
		943	939
	799	792	790
	581	566	556
		495	478
	268	280	268
a$_u$		968	969
	910	922	917
	589	622	610
		425	415
		172	168
b$_{3u}$	963	977	978
	839	855	853
	747	783	782
	708	732	730
	483	500	491
	218	210	206
		118	118
RMS error		22.4	21.8

[a] Observed and calculated frequencies by Cyvin *et al.* taken from [29]
[b] This work

Table 6 lists calculated and observed out–of–plane frequencies of pyrene. Cyvin's [29] and MO/8E results gave similar frequencies with average difference of 7.0 cm^{-1}. Both of these gave excellent RMS errors of ca. 22 cm^{-1}. As can be seen in Figure 4, RMS errors of out–of–plane frequencies for PAHs in the present MO/8E model were found to be ca. 20 cm^{-1}.

3.3 Ionic–State Planar Modes

Normal coordinate calculations for PAH ions can easily be made by the present MO/8E program. An optional parameter ION = +1 or −1 should be specified for positive or negative ion. BO and BBP values for ions are automatically processed via BO calculations with modified occupation numbers of electrons. As can be seen from Figure 6, RMS errors for ground–state planar frequencies of typical PAH cations are ca. 20 cm^{-1}. It should be noted that RMS errors are decreasing from naphthalene cation (26 cm^{-1}) to the larger cations (20–10 cm^{-1}). In the present MO/8E model, variations of force fields associated with loss of a π electron are only estimated from changes in BO and BBP. In this approximation, effects of loss of bonding electron are estimated to reduce CC stretching forces in average. However, it is well known that ionic characters strengthen

bonding forces to a certain extent. This latter effect is completely missing in the MO/8E treatments for ionic states. Thus, MO/8E frequencies for cations should be overestimated. Such an overestimation is expected to be the largest in naphthalene among various PAHs. In the larger PAHs, electron distribution caused by ionization becomes to be obscured because of much larger π electron delocalization, and thus RMS errors with respect to observed frequencies are decreasing. In view of this tendency, the MO/8E program can be applied to planar vibrations of PAH ions with an accuracy of ca. 20 cm^{-1}. A comparison with DFT calculations also supports this expectation. Table 7 lists calculated and observed [54,55] planar frequencies for anthracene. The average difference from the DFT B3LYP/6–31G(d) result with a scale factor of 0.956 was 20.0 cm^{-1}.

Table 7. Planar frequencies of anthracene cation C$_{14}$H$_{10}^+$ (cm^{-1}).

	DFT [b]	MO/8E [c]		Obs. [a]	DFT [b]	MO/8E [c]
a$_g$	1542	1555	b$_{1u}$	1586	1558	1566
	1482	1482		1418	1431	1440
	1364	1376		1291	1268	1293
	1237	1230			1256	1264
	1159	1179			1115	1115
	1012	1024			875	885
	733	733			638	656
	599	651			224	243
	379	375				
b$_{3g}$	1519	1528	b$_{2u}$	1541	1517	1520
	1498	1467		1430	1436	1433
	1377	1381		1364	1384	1378
	1254	1258		1341	1332	1335
	1167	1199		1188	1170	1170
	1078	1083			1146	1155
	884	890		1034	1012	1023
	495	548			799	817
	368	416			583	601
RMS error					19.4	15.0

[a] Observed infrared frequencies taken from [54,55]
[b] DFT B3LYP/6–31G(d) calculation with a scale factor of 0.956 by this work
[c] This work

The MO/8E program can also be used for normal coordinate calculations for PAH ions in excited states. Optional input data for this is only to specify the number of required electronic states from the lowest excited state. BO and BBP values for ions in excited states are automatically processed via BO calculations with modified occupation numbers of electrons. Since experimental data for molecular vibrations of excited PAH ions have been limited, evaluation of the present MO/8E program for excited ions will be made in subsequent reports.

3.4 Excited–State Planar Modes

Excited–state planar modes for neutral PAH molecules can be calculated by the present MO/8E program, in which excited–state properties are treated by the PPP–SCFMO–CI method. Figure 7 compares RMS errors for the present MO/8E calculations using excited–state BO and BBP with

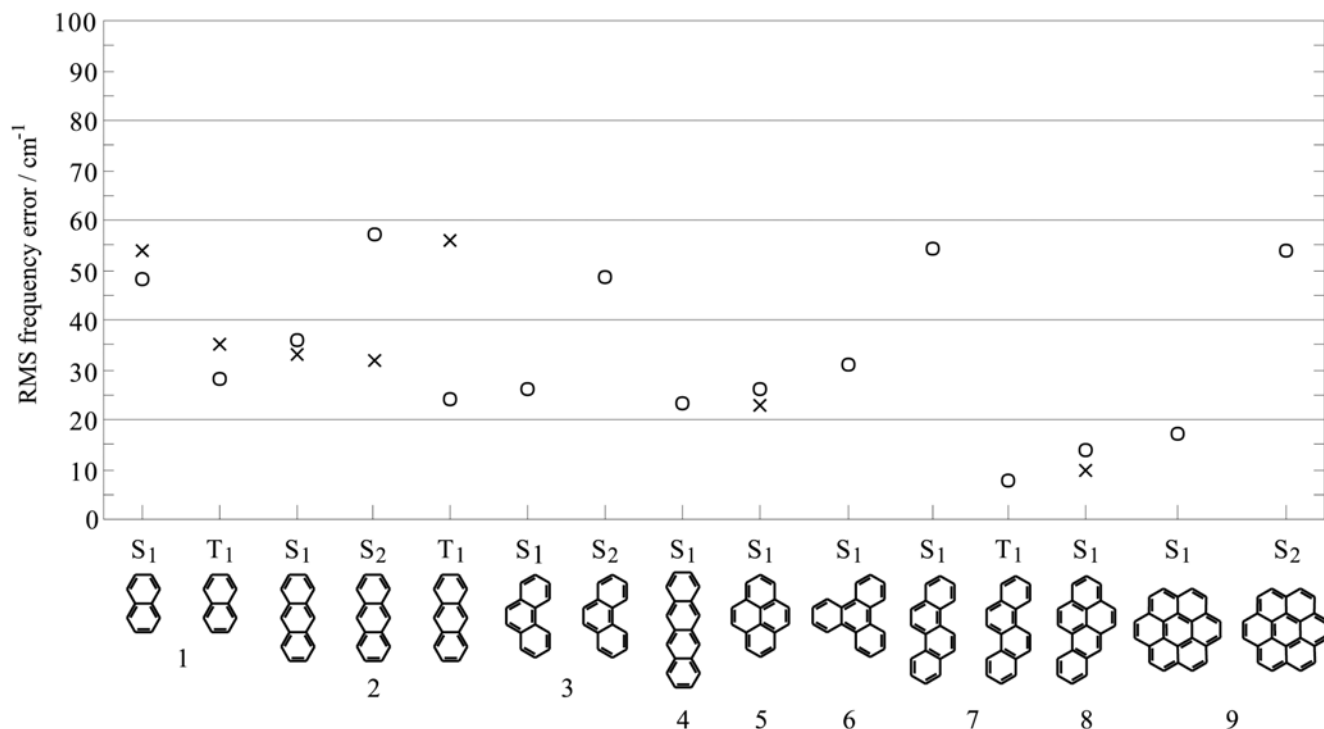those for *ab initio* configuration–interaction–singles (CIS) calculations [52,56–59].

Figure 7. A comparison of RMS frequency errors for excited–state vibrations. **1**. naphthalene $C_{10}H_8$; **2**. anthracene $C_{14}H_{10}$; **3**. phenanthrene $C_{14}H_{10}$; **4**. naphthacene $C_{18}H_{12}$; **5**. pyrene $C_{16}H_{10}$; **6**. triphenylene $C_{18}H_{12}$; **7**. chrysene $C_{18}H_{12}$; **8**. benzo[*a*]pyrene $C_{20}H_{12}$; **9**. pentacene $C_{22}H_{14}$; **10**. coronene $C_{24}H_{12}$. (○) The present MO/8E calculations. (×) CIS calculations for **1**, **2**, **5**, and **8** taken from [57,58], [52,56], [59], [59], respectively.

The CIS calculations gave RMS errors of 10–56 cm^{-1} with scale factors (0.89–0.90). The MO/8E approach with excited–state BO and BBP and without any other changes in the original MO/8 model gave RMS errors of 8–57 cm^{-1}. In the analyses to obtain Figure 7, we found some problems concerning with electronic and vibrational band assignments. The lowest excited singlet state of S_1 benzo[*a*]pyrene is ^1L_b, which is calculated in a very close vicinity of ^1L_a state possibly in reverse order, and thus the calculated state with a weak oscillator strength should be used for the comparison, as suggested by Goodpaster *et al*. [59]. In the case of the $S_2(^1L_a)$ state of coronene, the 0–0 band origin should be correctly assigned. In view of the vibronic activity of the L_a type transition to the ground state [17], we found that the 0–0 band of the $S_2(^1L_a)$–S_0 (^1A) transition should be assigned to a fluorescence excitation band at 28643 cm^{-1} based on the S_2–S_0 fluorescence [60]. Although study of excited–state assignments should be made more carefully, the MO/8E calculations of excited–state vibrations gave excellent RMS errors of 31.9 cm^{-1} in average for 214 modes, which is comparable with the CIS results of 30.7 cm^{-1} in average for 141 modes.

Table 8. Observed and calculated planar frequencies for the S_1 state of pyrene $C_{16}H_{10}$ (cm^{-1}).

	Obs. [a]	CIS [b]	MO/8 (BVDPS) [c]	MO/8E [d]		Obs. [e]	CIS [b]	MO/8E [d]
a_g		3015		3057	b_{2u}		3014	3056
		2998		3056			2987	3054
		2985		3055			2978	3054
	1629	1621	1626	1644			1536	1472
	1486	1502	1497	1516			1433	1398
	1424	1392	1436	1412			1340	1310
	1330	1288	1326	1310		1221	1227	1200
	1250	1237	1240	1233		1094	1046	1032
	1144	1135	1136	1140		1023	951	949
	1022	1017	1021	1028		820	782	796
	780	778	792	791		686	669	657
	572	545	576	575		471	482	515
	393	396	402	402	b_{1u}		2998	3056
b_{3g}		2992		3055			2990	3053
		2978		3054			1525	1484
	1573	1545	1568	1593			1470	1418
	1466	1467	1453	1464		1496	1429	1348
	1396	1409	1419	1381		1302	1284	1278
	1356	1380	1376	1359		1189	1188	1190
	1245	1242	1246	1245		1178	1146	1148
	1155	1162	1153	1157		1124	1098	1121
	1110	1095	1104	1098		924	912	935
	730	729	743	742		515	529	566
	494	495	528	528		339	348	363
	443	450	443	444				
RMS error		(17.3)[f]	(12.6)[f]	(14.7)[f]			23.3	25.7

[a] Observed frequencies taken from [43,62]
[b] CIS/3–21G frequencies with a scale factor of 0.89 taken from [59]
[c] MO/8 calculations taken from [43] by Borisevich *et al.*
[d] This work
[e] Observed frequencies taken from [61]
[f] RMS error for a_g and b_{3g} modes only

Table 8 lists observed [43,61,62] and calculated planar frequencies for the S_1 state of pyrene $C_{16}H_{10}$. CIS calculations by Goodpaster *et al.* [59] gave a RMS frequency error of 23.3 cm^{-1}, while the present MO/8E calculation yielded a RMS error of 25.7 cm^{-1}. Though vibrational modes are limited to a_g and b_{3g} types, Borisevich *et al.* [43] performed an analogous MO/8 calculation to yield a RMS error of 12.6 cm^{-1} with their experimental data, which should be compared with the RMS errors in parentheses for a_g and b_{3g} modes only, 17.3 cm^{-1} for CIS and 14.7 cm^{-1} for the present MO/8E.

3.5 Computational Efficiency

Since the MO/8E model is based on HMO and PPP calculations, its computational efficiency is remarkably higher than the conventional DFT and CIS calculations. Although it is not so straightforward to compare efficiencies of these methods, we have roughly compared computation time at central processing unit (CPU time). The ratios of CPU time for DFT B3LYP/6–31G(d)

normal coordinate calculations of the ground state with respect to those for the MO/8E were found to be ca. $1-5\times10^5$; for example, with a moderate size personal computer the DFT method required 35.5 days for normal coordinate calculations of tribenzophenalenyl radical $C_{25}H_{15}$, while the MO/8E spent only 15.42 seconds. In our experience, even with the commonly available supercomputer at a typical Synergy Center, it is only 10^2-10^3 times faster than a personal computer. In view of these situations, the present MO/8E model is promising for its application to very large PAHs and graphite fragments.

When one uses quantum chemical packages, one needs to construct input data of the molecular system. In the case of large molecules, it becomes a formidable task for the user to build up structural data either in Cartesian coordinates or in the Z–matrix form. For example, if the system has 100 atoms, ca. 300 data need to be prepared for the structural data. The present MO/8E program uses the rings input data, which considerably facilitate the use of this program.

4 CONCLUSIONS

The MO/8 model for normal coordinate calculations for PAHs was extended to include out–of–plane modes as well as to be applied to excited states and ionic states, and the new model was denoted as MO/8E. Molecular vibrations of PAHs can be predicted for both planar and out–of–plane modes in the ground state of any size of PAHs in the accuracy of ca. 20 cm^{-1}. Planar vibrations for ground–state ions can also be predicted in the accuracy of ca. 20 cm^{-1}. Excited–state planar vibrations can be predicted in the accuracy of ca. 30 cm^{-1}. Computation time of the MO/8E model is considerably smaller (ca. 10^{-5}) than conventional density functional and *ab initio* calculations. The MO/8E model is very efficient to predict molecular vibrations of PAHs without any data except for topological connections of hexagonal rings.

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Biographies

Koichi Ohno is Professor of Physical Chemistry at the Department of Chemistry, Graduate School of Science, Tohoku University. After obtaining a Ph.D. degree in Physical Chemistry of Science from the University of Tokyo in 1973, Dr. K. Ohno became a Ramsey memorial fellow at the University of Sheffield in UK for 1975–1977. Dr. K. Ohno has collaborated on Penning ionization studies with Professor Y. Harada at the University of Tokyo. After Dr. K. Ohno became Professor of the University of Tokyo in 1989 via Research Associate and Associate Professor, he moved to Tohoku University in 1994.

Risako Takahashi is a graduate student at the Department of Chemistry, Graduate School of Science in Tohoku University. She graduated from Department of Chemistry, Faculty of Science in the same university.

Megumi Yamada is a graduate student at the Department of Chemistry, Graduate School of Science in Tohoku University. She graduated from Department of Chemistry, Faculty of Science in the same university.

Yumiko Isogai is an undergraduate student at Department of Chemistry, Faculty of Science in Tohoku University.