Polycyclic Arenes

Infrared Spectra of Protonated Coronene and Its Neutral Counterpart in Solid Parahydrogen: Implications for Unidentified Interstellar Infrared Emission Bands**

Mohammed Bahou, Yu-Jong Wu, and Yuan-Pern Lee**

Abstract: *Large protonated polycyclic aromatic hydrocarbons (H$^+$PAHs) are possible carriers of unidentified infrared (UIR) emission bands from interstellar objects, but the characterization of infrared (IR) spectra of large H$^+$PAHs in the laboratory is challenging. IR absorption spectra of protonated coronene (1-C$_{24}$H$_{13}^+$) and mono-hydrogenated coronene (1-C$_{24}$H$_{13}$·), which were produced upon electron bombardment of parahydrogen containing a small proportion of coronene (C$_{24}$H$_{12}$) during matrix deposition, were recorded. The spectra are of a much higher resolution than those obtained by IR multiphoton dissociation by Dopfer and co-workers. The IR spectra of protonated pyrene and coronene collectively appear to have the required chromophores for features of the UIR bands, and the spectral shifts on an increase in the number of benzenoid rings point in the correct direction towards the positions of the UIR bands. Larger protonated peri-condensed PAHs might thus be key species among the carriers of UIR bands.*

The so-called unidentified infrared (UIR) emission bands of galactic and extragalactic objects show main features at 3.3, 6.2, 7.7, 8.6, and 11.2 μm.[1] Possible candidates for the carriers of these UIR bands include polycyclic aromatic hydrocarbons (PAHs) and their derivatives.[2] Protonated PAHs (H$^+$PAHs), especially the larger ones, were proposed because proton sources that could protonate PAHs are abundant in space, and H$^+$PAHs are stable closed-shell molecules.[3–5] To assess this hypothesis, a systematic investigation of the IR spectra of H$^+$PAHs for the comparison with UIR bands of interstellar media is essential. The characterization of the IR spectra of large H$^+$PAHs in the laboratory is challenging, partly because of the difficulties in generating H$^+$PAHs in sufficient quanti-

[*] Dr. M. Bahou, Prof. Y.-P. Lee
Department of Applied Chemistry and
Institute of Molecular Science
National Chiao Tung University
1001 Ta-Hsueh Rd., Hsinchu 30010 (Taiwan)
E-mail: yplee@mail.nctu.edu.tw

Dr. Y.-J. Wu
National Synchrotron Radiation Research Center
101, Hsin-Ann Road, Hsinchu 30076 (Taiwan)
E-mail: yjwu@nsrrc.org.tw

ties for spectral interrogation and partly because of the complicated nature of the spectra. Two major techniques are employed to characterize IR spectra of H$^+$PAHs. One method employs IR multiphoton dissociation (IRMPD) of H$^+$PAHs and monitors the loss of the H atom or the H$_2$ molecule upon exposure to light from a free-electron laser or an intense IR laser; the H$^+$PAH is produced and stored in an ion trap.[6,7] The spectral features of a spectrum that was obtained with the IRMPD technique are typically broad and red-shifted. The second method entails recording IR photodissociation action spectra of jet-cooled H$^+$PAHs that are tagged with a weakly bound ligand, such as argon, and monitoring the loss of the ligand upon irradiation of the tagged H$^+$PAH with an IR laser.[8–10] As the perturbation imposed by argon is small, the action spectrum of the argon-tagged H$^+$PAH is expected to be similar to the IR spectrum of the bare H$^+$PAH. The action spectrum thus obtained typically shows lines that are much narrower than those obtained by IRMPD, but the observed relative intensities in the action spectrum might not reflect the true IR intensities; furthermore, it is difficult to tag a ligand to large H$^+$PAHs that have excessive internal energy. The largest Ar-tagged H$^+$PAH that has been investigated with this method is protonated naphthalene (C$_{10}$H$_9^+$).[10]

Coronene (C$_{24}$H$_{12}$) is a peri-condensed PAH with seven benzenoid rings of D_{6h} symmetry. It serves as a prototype for an investigation of the roles of large PAHs in the interstellar medium.[11,12] It also catalyzes the production of H$_2$ under interstellar conditions because of its near-zero barrier for hydrogen addition.[13,14] Coronene may be protonated or hydrogenated at three distinct sites (Supporting Information, Figure S1). The most stable isomer of protonated coronene (C$_{24}$H$_{13}^+$) is 1-C$_{24}$H$_{13}^+$, which is protonated at a carbon atom on the outer unfused edge. The 2a-C$_{24}$H$_{13}^+$ cation, for which the protonation site is at a carbon on the outer fused edge, lies higher in energy than 1-C$_{24}$H$_{13}^+$ by approximately 65 kJ mol^{-1}.[13] The 2a'-C$_{24}$H$_{13}^+$ cation, with the protonation site at a carbon atom on the inner hexagon, is about 85 kJ mol^{-1} higher in energy than 1-C$_{24}$H$_{13}^+$.[13] With the IRMPD technique, Dopfer and co-workers reported the only IR spectrum of C$_{24}$H$_{13}^+$, which showed several overlapping broad features at 600–1800 cm^{-1}; these features lie near the features of the UIR bands.[5] Garkusha et al.[15] recorded the electronic absorption spectra of C$_{24}$H$_{13}^+$ and mono-hydro-genated coronene (C$_{24}$H$_{13}$·) in a neon matrix. They also measured the dispersed fluorescence of C$_{24}$H$_{13}^+$ in a neon matrix,[16] from which they determined vibrational wave-numbers of 16 modes of C$_{24}$H$_{13}^+$ in the X ^{1}A' state by comparing the spacing of the observed lines from the transition origin with vibrational wavenumbers predicted

with the B3LYP/cc-pVDZ method. The IR spectrum of $C_{24}H_{13}^{\cdot}$ has not been reported to date.

We have developed a method to investigate the IR spectra of H^{+}PAHs and their neutral counterparts that entails electron bombardment during matrix deposition of para-hydrogen (p-H_2) that contains a PAH in a small proportion. With this technique, we previously obtained high-resolution IR spectra of the protonated forms of benzene ($C_6H_7^+$),[17] naphthalene (1- and 2-$C_{10}H_9^+$),[18] and pyrene (1-$C_{16}H_{11}^+$),[19] as well as of their neutral counterparts. We demonstrated that this method is clean as it produces mainly the protonated parent and its neutral counterpart without fragmentation. Furthermore, the IR spectra, which display true IR intensities, small widths, excellent signal-to-noise ratios, and wide spectral coverage, are much superior to those obtained from IRMPD and IR dissociation of argon-tagged species.

According to an astrochemical model, PAHs that contain 20–130 carbon atoms are likely candidates for carriers of UIR bands because they are photochemically stable in interstellar clouds.[20] Continuing our systematic investigations of the IR spectra of H^{+}PAHs, we applied our method to record the IR absorption spectrum of a larger H^{+}PAH, namely protonated coronene ($C_{24}H_{13}^+$).

A partial IR spectrum of a $C_{24}H_{12}$/p-H_2 (1:1500) matrix that was bombarded with electrons during deposition is shown in Figure 1 a (for spectra covering a wider region, see Figure S2–S4). The IR spectrum of a $C_{24}H_{12}$/p-H_2 (1:1500)
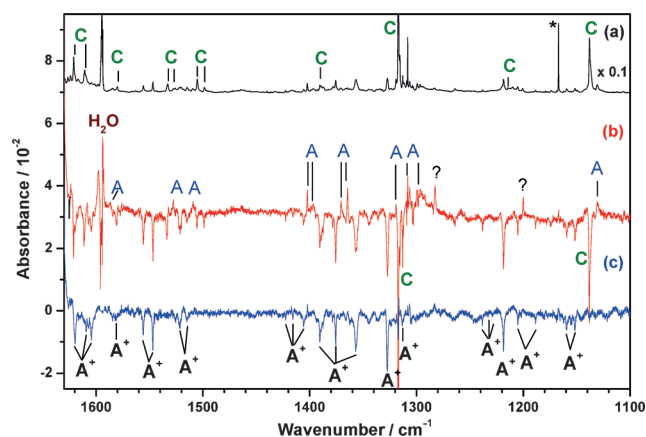

Figure 1. Partial IR spectra of electron-bombarded coronene. a) An electron-bombarded matrix of $C_{24}H_{12}$/p-H_2 (1:1500). b) A difference spectrum of the matrix sample upon irradiation at 365 nm for 2.5 h. c) A difference spectrum of a $C_{24}H_{12}$/p-H_2 (1:1500) matrix, which was kept in the dark for 10 h in a separate experiment. C = $C_{24}H_{12}$, A[+] = 1-$C_{24}H_{13}^+$, A = $C_{24}H_{13}^{\cdot}$, * = p-H_2 absorption, ? = unidentified species.

matrix that was not subjected to electron bombardment is shown in Figure S5; the observed line positions are compared with those reported for the Ar matrix and with those that were calculated quantum-chemically (Table S1). Scaling factors of 0.958 and 0.978 for the CH stretching modes (2800–3300 cm^{-1}) and other regions, respectively, were derived by comparing the observed lines with theoretical predictions to achieve the best fit. Unmarked weaker features (Figure 1 a)

are due to species that were produced on electron bombardment. To distinguish these features, we irradiated the matrix at 365 nm for 2.5 h and plotted the difference spectrum, which was obtained on subtracting the spectrum recorded before irradiation from that recorded after irradiation (Figure 1 b); lines pointing upwards indicate production, whereas those pointing downwards indicate destruction. Irradiation of the matrix with UV light is expected to release electrons trapped in the matrix, which results in the neutralization of cations;[17–19] photodissociation or photoisomerization might also occur. Without irradiation, the trapped electrons diffuse slowly and might recombine with the cations to form neutral species. In a separate experiment, we maintained the matrix in darkness for 10 h, and plotted the difference spectrum (Figure 1 c). The spectrum is similar to that recorded upon UV irradiation except that the intensities of upward-pointing features are weaker and the downward-pointing features of coronene that arise from UV photolysis are nearly absent.

The features that are shown in Figure 1 b and 1 c are classified into three groups according to the correlated intensity alterations at various stages of the experiments. The features that point downwards in Figure 1 b, but are missing in Figure 1 c are due to coronene (C); some of these features show a first-derivative shape because of a small shift in line position. The downward features (A[+]; Figure 1 b,c) with intense lines at 1619.7, 1546.8, 1375.7, 1356.7, 1327.2, 1218.5, and 874.0 (not shown) cm^{-1} are likely associated with a cationic species reacting with electrons in p-H_2. These features are assigned to 1-$C_{24}H_{13}^+$ (see below). The upward features (A; Figure 1 b,c) with intense lines at 1364.5, 1308.2, and 1296.8 cm^{-1} are likely associated with a neutral species that is produced by the reaction of an electron with a cation. Additional intense features at 1003.4, 851.1, 847.2, 822.4, and 541.0 cm^{-1} are shown in Figure S4. These features are assigned to 1-$C_{24}H_{13}^{\cdot}$ (see below). Four upward-pointing lines at 1282.3, 1200.4, 1039.3, and 968.5 cm^{-1} (?; Figure 1 b) that belong to none of these three groups may currently not be positively identified.

The IRMPD spectrum of $C_{24}H_{13}^+$ is shown in Figure 2 a.[5] In Figure 2 b, the inverted version of the spectrum in Figure 1 c is shown, and lines that belong to the group A[+] are indicated with arrows. The spectra of 1-$C_{24}H_{13}^+$, 2a-$C_{24}H_{13}^+$, and 2a′-$C_{24}H_{13}^+$ were simulated according to the scaled vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d,2p) method (Figure 2 c–e); the same scaling factors as for coronene were used. Calculated harmonic vibrational wavenumbers (scaled) and IR intensities of 1-$C_{24}H_{13}^+$ are presented in Table S2; the corresponding values for 2a-$C_{24}H_{13}^+$ and 2a′-$C_{24}H_{13}^+$ are given in Table S3.

On comparison of Figure 2 b with Figure 2 c–e, the observed features clearly agree best with those predicted for 1-$C_{24}H_{13}^+$, rather than with those of 2a-$C_{24}H_{13}^+$ or 2a′-$C_{24}H_{13}^+$; in particular, in the spectral region of 1300–1600 cm^{-1}, the absorption lines of these three isomers are distinct. Some representative lines of A[+] are compared with theoretical predictions and fluorescence spacing[16] in Table S4; a list of all observed lines is available in Table S2. Deviations between observed and predicted (scaled) vibrational wavenumbers of 1-$C_{24}H_{13}^+$ are within 13 cm^{-1} (0.9 %), and nearly all features
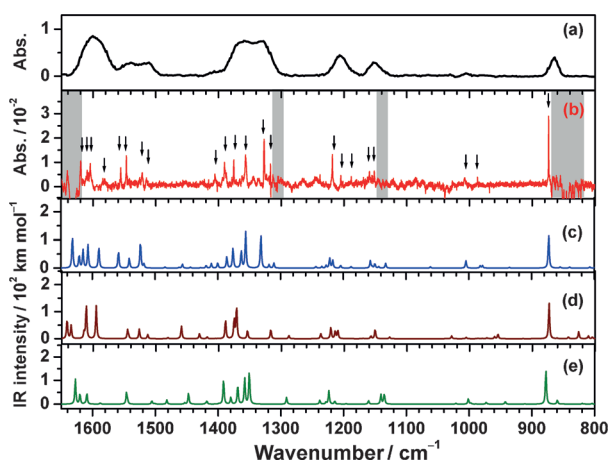
Figure 2. Comparison of observed and predicted IR spectra for $C_{24}H_{13}^+$. a) Spectrum of $C_{24}H_{13}^+$ recorded with the IRMPD method.[5] b) Spectrum of lines in group A^+ ($\downarrow$), taken from Figure 1 c and inverted; regions for which the absorption of coronene interferes are marked with light grey. c–e) Spectra of 1-$C_{24}H_{13}^+$, 2a-$C_{24}H_{13}^+$, and 2a′-$C_{24}H_{13}^+$, simulated according to scaled vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311 + + G(2d,2p) method.

with a predicted IR intensity of greater than 9 km mol^{-1} in the probed spectral region were observed.

The features obtained with the IRMPD method are broad and contain limited information for spectral identification, but the general contours satisfactorily agree with the IR features recorded in this work, except for slight red shifts that are due to anharmonic effects (Figure 2a). As our spectral resolution is much greater than in IRMPD experiments, the observed lines were unambiguously assigned to the corresponding vibrational modes of a specific isomer, namely 1-$C_{24}H_{13}^+$.

Lines in group A are likely correlated with the neutral form (1-$C_{24}H_{13}^{\cdot}$) because conversion from lines in group A^+ (1-$C_{24}H_{13}^+$) to group A was observed upon irradiation or after maintaining the matrix in darkness (for detailed assignments, see the Supporting Information). A comparison of the observed lines in group A with spectra of 1-$C_{24}H_{13}^{\cdot}$, 2a-$C_{24}H_{13}^{\cdot}$, and 2a′-$C_{24}H_{13}^{\cdot}$ that were simulated according to predicted scaled vibrational frequencies and IR intensities is shown in Figure S6 and Tables S5–S7. The identification of the IR spectrum of 1-$C_{24}H_{13}^{\cdot}$ is new.

The IR spectra of H$^+$PAHs show a strong dependence not only on the number of aromatic rings, but also on the framework of the fused rings. Linear H$^+$PAHs are excluded as carriers of UIR bands because reported IRMPD spectra of these cata-condensed H$^+$PAHs with one to five aromatic rings showed several intense features at 6.5–7.2 μm, where no obvious UIR bands are observed; the characteristic UIR bands near 7.7 and 11.2 μm were also not observed for these compounds.[7] In contrast, reported IRMPD spectra of protonated pyrene and coronene[5,7] showed absorption bands near the UIR bands, but the broad IRMPD action spectra provided insufficient information on the trend of changes in relative intensities and line positions of the corresponding fundamental vibrational modes.

Our absorption spectra, which were obtained at greater resolution with true IR intensity, provide useful information for comparison with UIR bands. The matrix shifts that are induced by p-H$_2$ are similar to those induced by argon and typically smaller than 1% from the values of the gaseous phase; hence the small shifts on our observed lines negligibly affect the comparison with the broad UIR features. We have recorded the IR absorption spectra of H$^+$PAHs according to the evolution of the circumferential growth of the PAHs, from benzene to coronene. The IR absorption spectra of protonated benzene, naphthalene, pyrene, and coronene, which were isolated in solid p-H$_2$, were compared with the UIR spectrum of the photodissociation region at the Orion Bar (Figure S7;[2] for lists of observed lines of $C_6H_7^+$, 1-$C_{10}H_9^+$, 1-$C_{16}H_{11}^+$, and 1-$C_{24}H_{13}^+$, see Table S8). A survey of these experimental results shows that all these protonated species have IR features near 6.2 μm, which are characteristic of the CC stretching mode of aromatic rings, shift insignificantly as the size increases. For 1-$C_{24}H_{13}^+$, three major lines in the 7–9 μm region appear at 7.37, 7.53, and 8.21 μm and correspond to red shifts of the bands of 1-$C_{16}H_{11}^+$ at 7.19, 7.45, and 8.13 μm; they are near the UIR bands at approximately 7.6, 7.8, and 8.6 μm. These three modes correspond to ring deformation, CH$_2$ scissoring, and in-plane CH bending modes, respectively; the second one is unique and characteristic of H$^+$PAHs. In contrast, the line at 11.5 μm, which corresponds to the out-of-plane CH bending mode of 1-$C_{16}H_{11}^+$, is blue-shifted to 11.4 μm for 1-$C_{24}H_{13}^+$, but approaches the UIR band near 11.2 μm. These four lines are either weak or absent for protonated benzene and naphthalene; they become prominent only for larger H$^+$PAHs, such as pyrene and coronene.

The IR features of protonated pyrene and coronene collectively appear to have the required chromophores to account for prominent features of UIR bands, and the spectral shifts on an increase in the number of aromatic rings point in the correct direction towards the positions of the UIR bands. Larger protonated peri-condensed PAHs might thus be important carriers of UIR bands.

Experimental Section

A gold-plated copper plate that was cooled to 3.2 K served as a cold substrate for our matrix samples.[21] The substrate was cooled with a closed-cycle helium refrigerator system (Janis RDK-415). $C_{24}H_{13}^+$ and $C_{24}H_{13}^{\cdot}$ were produced on electron bombardment of a gaseous sample during deposition of p-H$_2$ containing a small percentage of coronene ($C_{24}H_{12}$). A gaseous mixture of $C_{24}H_{12}$/p-H$_2$ (1:1500) was deposited, typically over a period of 7 h at a flow rate of ca. 13 mmol h^{-1}. An electron beam at 250 eV and 60 μA was generated with an electron gun (Kimball Physics, Model EFG-7).[17–19] Electron bombardment of p-H$_2$ produced H$_2^+$, which further reacted with H$_2$ to produce H$_3^+$ and H. $C_{24}H_{13}^+$ was presumely produced on proton transfer from H$_3^+$, and $C_{24}H_{13}^{\cdot}$ is produced either on neutralization of $C_{24}H_{13}^+$ or on reaction of $C_{24}H_{12}$ with H. A light-emitting diode (LED) with an emission wavelength of 365 ± 10 nm was employed for further photolysis. For the production of $C_{24}H_{13}$, a separate experiment using Cl$_2$/$C_{24}H_{12}$/p-H$_2$ (3:2:2000) without electron bombardment was also carried out. The matrix was irradiated with the LED at 365 nm for 2 h to generate Cl atoms, which was followed by irradiation with IR light for 2 h to activate the reaction of Cl and

H_2 to produce H atoms[22] to react with $C_{24}H_{12}$. Normal H_2 (99.9999%, Scott Specialty Gases) was passed through a trap at 77 K before entering a p-H_2 converter containing an iron(III) oxide catalyst (Aldrich) and cooled with a closed-cycle refrigerator. The conversion efficiency was controlled by the temperature of the catalyst; at 11–13 K, o-H_2 levels were less than 100 ppm. Coronene (95%, Tokyo Chemicals) was heated to 425 K to increase its vapor pressure during deposition. IR absorption spectra covering a spectral range of 450–5000 cm^{-1} were recorded with a Fourier-transform infrared (FTIR) spectrometer (Bomen DA8) equipped with a KBr beam splitter and a HgCdTe detector at 77 K. Typically, 600 scans at a resolution of 0.25 cm^{-1} were recorded at each stage of the experiment.

Energies, equilibrium structures, vibrational wavenumbers, and IR intensities were calculated with the Gaussian 09 program.[23] Density functional theory calculations were performed using the B3PW91 method with Becke's three-parameter hybrid exchange functional[24] and the exchange functional of Perdew and Wang as the correlation functional.[25] The standard basis set 6-311++G(2d,2p) was used.

[1] "PAHs and the Universe": A. G. G. M. Tielen, *EAS Publication Series*, *Vol. 46* (Eds.: C. Joblin, A. G. G. M. Tielens), EAD Sciences, Les Ulis, France, **2011**, pp. 3–10.

[2] "PAHs and the Universe": E. Peeters, *EAS Publication Series*, *Vol. 46* (Eds.: C. Joblin, A. G. G. M. Tielens), EAD Sciences, Les Ulis, France, **2011**, pp. 13–27.

[3] V. Le Page, Y. Keheyan, V. M. Bierbaum, T. P. Snow, *J. Am. Chem. Soc.* **1997**, *119*, 8373–8374.

[4] T. P. Snow, V. Le Page, Y. Keheyan, V. M. Bierbaum, *Nature* **1998**, *391*, 259–260.

[5] "PAHs and the Universe": O. Dopfer, *EAS Publication Series*, *Vol. 46* (Eds.: C. Joblin, A. G. G. M. Tielens), EAD Sciences, Les Ulis, France, **2011**, pp. 103–108.

[6] W. Jones, P. Boissel, B. Chiavarino, M. E. Crestoni, S. Fornarini, J. Lemaire, P. Maitre, *Angew. Chem.* **2003**, *115*, 2103–2105; *Angew. Chem. Int. Ed.* **2003**, *42*, 2057–2059.

[7] H. Knorke, J. Langer, J. Oomens, O. Dopfer, *Astrophys. J. Lett.* **2009**, *706*, L66–L70.

[8] N. Solcà, O. Dopfer, *Angew. Chem.* **2002**, *114*, 3781–3784; *Angew. Chem. Int. Ed.* **2002**, *41*, 3628–3631.

[9] G. E. Douberly, A. M. Ricks, P. v. R. Schleyer, M. A. Duncan, *J. Phys. Chem. A* **2008**, *112*, 4869–4874.

[10] A. M. Ricks, G. E. Douberly, M. A. Duncan, *Astrophys. J.* **2009**, *702*, 301–306.

[11] J. L. Weisman, T. J. Lee, F. Salama, M. Head-Gordon, *Astrophys. J.* **2003**, *587*, 256–261.

[12] A. Pathak, P. J. Sarre, *Mon. Not. R. Astron. Soc.* **2008**, *391*, L10–L14.

[13] M. Hirama, T. Tokosumi, T. Ishida, J.-I. Aihara, *Chem. Phys.* **2004**, *305*, 307–316.

[14] E. Pauls, L. Hornekaer, *Astrophys. J.* **2008**, *679*, 531–536.

[15] I. Garkusha, J. Fulara, P. J. Sarre, J. P. Maier, *J. Phys. Chem. A* **2011**, *115*, 10972–10978.

[16] I. Garkusha, J. Fulara, J. P. Maier, *J. Mol. Struct.* **2012**, *1025*, 147–150.

[17] M. Bahou, Y.-J. Wu, Y.-P. Lee, *J. Chem. Phys.* **2012**, *136*, 154304.

[18] M. Bahou, Y.-J. Wu, Y.-P. Lee, *Phys. Chem. Chem. Phys.* **2013**, *15*, 1907–1917.

[19] M. Bahou, Y.-J. Wu, Y.-P. Lee, *J. Phys. Chem. Lett.* **2013**, *4*, 1989–1993.

[20] A. G. G. M. Tielens, *Annu. Rev. Astron. Astrophys.* **2008**, *46*, 289–337.

[21] Y.-P. Lee, Y.-J. Wu, R. M. Lees, L.-H. Xu, J. T. Hougen, *Science* **2006**, *311*, 365–368.

[22] M. Bahou, J.-Y. Wu, K. Tanaka, Y.-P. Lee, *J. Chem. Phys.* **2012**, *137*, 084310.

[23] GAUSSIAN 09, Revision A.02, M. J. Frisch et al. Gaussian, Inc., Wallingford, CT, USA, **2009**.

[24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[25] J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533–16539.