Pergamon

TUNNELING ACROSS MOLECULAR WIRES: AN ANALYTICAL EXACTLY SOLVABLE MODEL

Alexander Onipko,[a],* Yuriy Klymenko,[b] Lyuba Malysheva[a] and Sven Stafström[c]

[a]Bogolyubov Institute for Theoretical Physics, Kiev, 252143, Ukraine
[b]Space Research Institute, Kiev, 252022, Ukraine
[c]Department of Physics, IFM, Linköping University, S-581 83 Linköping, Sweden

On the basis of the Landauer approach and Green function technique we have developed an exactly solvable analytical model that gives a quick and reliable estimate of (ohmic) tunnel conductance in metal–molecular heterojunctions. The model covers conjugated oligomers of types $M–M–\cdots–M$ and $M_1–M_2–M_1–\cdots–M_2–M_1$ connecting metal pads in molecular contacts. Based on a realistic Hamiltonian for these kinds of oligomers we obtain an analytical expression for the tunnel conductance: $(2e^2/h)g_0(E_F)g_0^{mol}(E_F)e^{-2\delta(E_F)N}$, where N is the number of the structural units M (or M_1). The pre-exponential factor $g_0(E_F)$ depends on the metal and metal–molecule coupling characteristics only, whereas $g_0^{mol}(E_F)$ and the exponential decay constants are explicit functions of the Green function matrix elements of monomers M (or M_1 and M_2). This formula provides, for the first time, an analytical relationship between a realistic description of the molecular electronic structure and the heterojunction resistance. The results obtained from this formula are of immediate use for probing currents through single molecules, e.g. by scanning tunneling microscope (STM) techniques as well as for measurements of electron transfer rates in donor/bridge/acceptor systems. © 1998 Published by Elsevier Science Ltd

Keywords: A. nanostructures, A. surfaces and interfaces, D. electronic transport, D. tunneling.

The recent development of different kinds of nanotechnologies and chemical synthesis has led to a dramatic increase in the research interest in molecular size devices [1, 2] and metal–molecular heterojunctions [3–5]. Along with the experimental advancements, there is also a need for a deeper theoretical understanding of this type of systems. So far, most theoretical studies have been based on numerical calculations of, for instance, the conductance through single molecular wires [5–7]. In this Letter we present a complementary approach, an exact analytical solution of the problem of tunnel conductance in metal-molecular heterojunctions where linear molecules with negligible transverse interaction act as molecular wires. Unlike previous attempts in this direction [8, 9] this solution provides a direct relationship between the conducting properties of molecular wires and their electronic structure.

Our model is based on a Su–Schrieffer–Heeger (SSH) type of Hamiltonian that has been shown to give an adequate description of a number of fundamental properties of conducting polymers [10]. The one-electron Hamiltonian describing the π electron manifold of (M)-oligomers, linear conjugated molecules of type $M–M–\cdots–M$ with the rigid backbone can be represented as

$$\hat{H}^{O_M} = \sum_{n=1}^{N}(\hat{H}_n^M + \beta_i|(n \pm 1)_{\alpha_{l(r)}}\rangle\langle n_{\alpha_{r(l)}}|), \qquad (1)$$

where index $l(r)$ refers to the upper (lower) sign, $|0_{\alpha_r}\rangle = |(N + 1)_{\alpha_l}\rangle = 0$. Ket $|n_\alpha\rangle$ has its usual meaning of the $2p_z$ atomic orbital of the αth atom in the nth
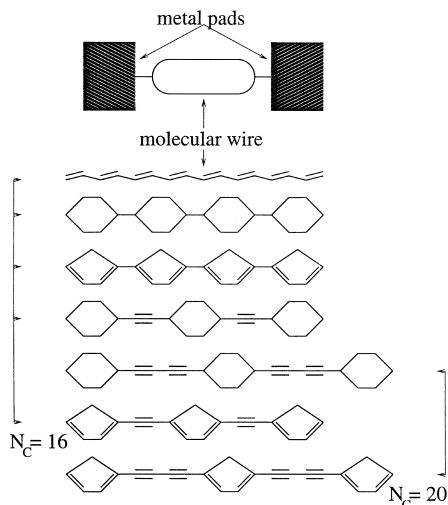
* Corresponding author.

Fig. 1. Schematic representation of metal–molecular heterojunction (top) and the structure of conjugated oligomers considered here as molecular wires. N_C refers to the number of C atoms in row.

monomer. The monomer π electron Hamiltonian is $\hat{H}_n^M$ and β_i is the $2p_z$ resonance energy (hopping integral) between the neighboring sites (denoted α_l and α_r, respectively) of adjacent monomers.

Using the Landauer approach [11], the conductance g is expressed in terms of the transmission coefficient $T(E_F)$ at the Fermi energy E_F as: $g = (2e^2/h)T(E_F)$. For the model of metal-molecular structure shown in Fig. 1, $T(E_F)$ takes the form [8]

$$T(E_F) = A_1(E_F)A_N(E_F)|G_{1_{\alpha_l}, N_{\alpha_r}}(E_F)|^2, \qquad (2)$$

where $A_{1(N)}(E_F)$ is the spectral density of the left (right) metal pad [8] and $G_{1_{\alpha_l}, N_{\alpha_r}}(E_F)$ is the dimensionless (multiplied by β_i) matrix element of the system (metal–molecule–metal) Green function.

Finding the Green function in equation (2) by analytical methods presents a quite complex task. Thus far, this problem has been solved under reasonable assumptions regarding metal pads but only for the simplest model of a linear chain of one-level subunits, C atoms, coupled via a constant nearest-neighbor interaction β_i [8]. The model is, however, too simple to provide a realistic description of the electronic structure of the oligomers of interest for molecular devices. In particular, it cannot describe the electron tunneling through band gaps, which is believed to be the most likely mechanism of molecular wire resistance [6, 7], since it does not lead to a band gap in the molecule electron spectrum. In contrast, there are numerous successful treatments on the basis of SSH Hamiltonian, which by a proper choice of $\hat{H}_n^M$ and β_i lead to a realistic description of the electronic spectrum of conjugated oligomers. (To a certain extent the modification of the

molecule electron spectrum due to metal-molecule interaction can also be taken into account in equation (1). In this sense, the term molecule in the present context should be understood conditionally.) Since the derivation of the conductance formula does not depend on the detailed form of $\hat{H}_n^M$ in equation (1), we do not specify it further at this point in the presentation. Instead we proceed by applying the Green function technique to arrive at an analytical expression of tunnel conductance in terms of the monomer Green function.

1. TUNNEL CONDUCTANCE

We can show that for a molecule of arbitrary complexity the Green function matrix element appearing in equation (2) is substantially dependent on the metal and contact characteristics only when the transmission coefficient is close to its maximal value (for the model of symmetrical heterojunctions at hand $T_{max}(E_F) = 1$). If, on the other hand, $T_{max}(E_F) \ll 1$ equation (2) can be reduced to

$$T(E_F) = A_1(E_F)A_N(E_F)[G_{1_{\alpha_l}, N_{\alpha_r}}^{O_M}(E_F)]^2, \qquad (3)$$

where, as distinct from equation (2), $G^{O_M}(E_F)$ is the oligomer (and not the system) Green function. The validity of approximation (3) can of course be verified by checking that the inequality $T(E_F) \ll 1$ is satisfied. Note that the spectral densities, $A_1(E_F)$ and $A_N(E_F)$, that play the role of effective metal–molecule coupling constants, do not need to be small. The property $T(E_F) \ll 1$ is related to the fact that we are studying electron transmission due to tunneling across the molecule, i.e. transmission at energies that coincide with the gap in the energy spectrum of the molecules. In addition to the requirement that $T(E_F) \ll 1$, for the replacement of equation (3) with equation (2) we also have to exclude the case of localized levels in the gap studied in [12, 13].

The replacement of the system Green function in equation (2) by the molecule Green function limits our attention to the case, where the Fermi energy is within a band gap of the molecule, likely, the HOMO-LUMO gap [6, 7] (HOMO is the highest occupied molecular orbital, LUMO is the lowest unoccupied molecular orbital).

Calculation of the conductance is now reduced to the problem of finding the solution to the equation $(E\mathbf{I} - \mathbf{H}^{O_M})\mathbf{G}^{O_M}(E) = \beta_i\mathbf{I}$. With the Hamiltonian defined in (1) we obtain for the matrix element $G_{1_{\alpha_l}, N_{\alpha_r}}^{O_M}(E)$ of matrix $\mathbf{G}^{O_M}(E)$

$$G_{1_{\alpha_l}, N_{\alpha_r}}^{O_M}(E) = \frac{G_{\alpha_l, \alpha_r}^M \sin\xi}{\sin(\xi N) - G_{\alpha_l, \alpha_r}^M \sin[\xi(N-1)]}, \qquad (4)$$

where $G_{\alpha, \alpha'}^M = \langle\alpha|\beta_i/(E\hat{I} - \hat{H}_n^M)|\alpha'\rangle$ (we omit the indication of explicit dependence of monomer Green function

on energy) and ξ is determined by the dispersion law

$$2 \cos \xi = f(E). \tag{5}$$

In the case of the C-chain model, $f(E) = E/\beta_i$ (with the on-site electron energy at C atom set equal to zero). But for realistic oligomers, such as those shown in Fig. 1, the function $f(E) \to f_{O_M}(E)$ is determined by [12]

$$G^M_{\alpha_l,\alpha_r} f_{O_M}(E) = 1 - G^M_{\alpha_l,\alpha_l} G^M_{\alpha_r,\alpha_r} + (G^M_{\alpha_l,\alpha_r})^2. \tag{6}$$

Equations (4)–(6) give an exact closed expression for $G^{O_M}_{1_{\alpha_l},N_{\alpha_r}}(E)$ in terms of the monomer Green function matrix elements. By standard methods the knowledge of $\mathbf{G}^{O_M}(E)$ can be extended to cover $(M_1\text{-}M_2)$-oligomers consisting of the linear sequence of $N - 1$ identical monomers $M = M_1\text{-}M_2$ ended by "defect" M_1, i.e. the molecules of type $M_1\text{–}M_2\text{–}M_1\text{–}\cdots\text{–}M_2\text{–}M_1$. In particular, we obtain the analogue of equation (4) for the Green function matrix element $G^{O_{M_1\text{-}M_2}}_{1_{\alpha_l},N_{\alpha_r}}(E)$ of $\mathbf{G}^{O_{M_1\text{-}M_2}}(E)$ in the form

$$G^{O_{M_1\text{-}M_2}}_{1_{\alpha_l},N_{\alpha_r}}(E) = \frac{G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_{\alpha_l,\alpha_r} \sin \xi}{G^{M_2}_{\alpha_l,\alpha_r}(E) \sin(\xi N) + G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_\Delta \sin[\xi(N-1)]}, \tag{7}$$

where

$$G^{M_1(M_2)}_\Delta = G^{M_1(M_2)}_{\alpha_l,\alpha_l} G^{M_1(M_2)}_{\alpha_r,\alpha_r} - (G^{M_1(M_2)}_{\alpha_l,\alpha_r})^2,$$

and ξ is determined from dispersion relation (5), where $f(E) \to f_{O_{M_1-M_2}}(E)$ is given by [12]

$$G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_{\alpha_l,\alpha_r} f_{O_{M_1-M_2}}(E) = 1 - G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_{\alpha_r,\alpha_r} - G^{M_2}_{\alpha_l,\alpha_l} G^{M_1}_{\alpha_r,\alpha_r}$$
$$+ G^{M_1}_\Delta G^{M_2}_\Delta. \tag{8}$$

For in-gap (or out-of-band) energies defined in the limit $N \to \infty$ the dimensionless wave vector ξ in (5) takes complex values $\xi = \pm i\delta$ or $\xi = \pi \pm i\delta$, $\delta > 0$. Inserting these into equations (4), (5) and (7) results in an exponential dependence with the following definition of the decay constant $\delta \equiv \delta(E)$

$$\delta(E) = \ln \left| |f(E)|/2 + \sqrt{[f(E)/2]^2 - 1} \right|, \tag{9}$$

if $\delta(E)N \gg 1$. Thus the conductance can be expressed as (in units of $2e^2/h$):

$$g = g_0(E_F) g_0^{mol}(E_F) e^{-2\delta(E_F)N}, \tag{10}$$

where $g_0(E_F) = A_1(E_F) A_N(E_F)$,

$$g_0^{mol}(E_F) = \frac{4 \sinh^2[\delta(E_F)]}{([G^M_{\alpha_l,\alpha_r}]^{-1} \pm e^{-\delta(E_F)})^2} \tag{11}$$

for (M)-oligomers and

$$g_0^{mol}(E_F) = \frac{4(\sinh[\delta(E_F)]G^{M_2}_{\alpha_l,\alpha_r})^2}{(G^{M_2}_{\alpha_l,\alpha_r}/G^{M_1}_{\alpha_l,\alpha_r} \mp G^{M_2}_\Delta e^{-\delta(E_F)})^2}, \tag{12}$$

for $(M_1\text{-}M_2)$-oligomers; the upper sign refers to $\xi = \pi \pm i\delta$ and the lower sign corresponds to $\xi = \pm i\delta$.

The exponential decay constant $\delta(E_F)$ in equation (10) is nothing more than the modulus of the imaginary part of the (dimensionless) complex wave vector of an electron entering the molecule with the kinetic energy outside the electronic bands of the oligomer.

The pre-exponential factor in the tunnel conductance of metal–molecule interface defined in equation (10) has been intentionally represented as a product $g_0(E_F) \times g_0^{mol}(E_F)$ in order to separate the contribution coming from the molecule, $g_0^{mol}(E_F)$ which does not depend on the length of the molecular wire but does depend on E_F.

Furthermore, the energy dependence of both the decay constant and $g_0^{mol}(E_F)$ is expressed in terms of the monomer Green function only. Thus, it is possible to predict and understand the most essential charge transfer properties of potential molecular wires simply by studying the properties of the monomer building block(s).

Note that in the case of the C-chain model equations (9)–(11) restore the McConnell result referred to the non-adiabatic bridge-mediated electron transfer rate [14], $k_{ET} \sim e^{-2\delta(E)N}$, where $\delta(E) = \ln|E/\beta_i|$, for energies that are far from the band states, $|E/\beta_i| \gg 1$. This corner stone in the theory of non-adiabatic electron transfer is thus shown here to apply also to intra-molecular (oligomer) through-gap charge transport in conjugated systems, but with the generalized definitions of the decay constant and pre-exponential factor given in equations (9), (11) and (12). We stress that this result applies to any oligomer covered by structural formula $M\text{–}M\text{–}\cdots\text{–}M$ or $M_1\text{–}M_2\text{–}M_1\text{–}\cdots\text{–}M_2\text{–}M_1$, i.e. essentially, to all types of conjugated systems.

2. EXAMPLES OF MOLECULAR WIRES

Consider now some particular examples of (M)- and $(M_1\text{-}M_2)$-oligomers shown in Fig. 1: oligomers of polyene, $M = C_2H_2$; poly-paraphenylene, $M = C_6H_4$; polythiophene $M = C_4H_2S$; poly(paraphenylene-ethynylene), $M_1 = C_6H_4$, $M_2 = C_2$; poly(paraphenylene-butadiyne), $M_1 = C_6H_4$, $M_2 = C_4$; poly(thiophene–ethynylene), $M_1 = C_4H_2S$, $M_2 = C_2$; and poly(thiophene–butadiyne), $M_1 = C_4H_2S$, $M_2 = C_4$.

In Table 1 are shown the results obtained from equations (9)–(12). Only the maximal values of the decay constant in the HOMO-LUMO gap Δ_{HL} are presented, corresponding to the case when the conductance is minimal, $g = g_{min} = g_0^{mol}(\delta_{max}) e^{-2\delta_{max}N}$. (We set factor g_0 that is never known in real experiments to be equal to unity as probably, can be the case in best metal–molecular contacts.)

The parameters of the Hamiltonian of the oligomers $\hat{H}^{O_M}$ are defined as follows: In polyenes and five-membered ring based oligomers the hopping integrals associated with single and double and single and triple C–C bonds,

Table 1. Transport related quantities of the oligomers listed in Fig. 1 (presented here in the same order as in Fig. 1): maximal value of exponential decay constant δ_{max}, HOMO-LUMO gap Δ_{HL}; experimental estimates of the optical gap Δ_{HL}^{exp}, minimal tunneling conductance g_{min}. The oligomer length is indicated as $N_C = 16$, 20, 22 and 28, N_C is the number of C atoms in row, see Fig. 1

Oligomer	g_0^{mol} (δ_{max})	δ_{max}	Δ_{HL} (eV)	Δ_{HL}^{exp} (eV)	g_{min} (×10^{-2})				R_{max} (×10^2)			
					16	20	22	28	16	20	22	28
(M)												
M = C_2H_2	1	0.27	2.0	1.8 [17]	1.4	0.48	0.28	0.06	0.71	2.08	3.57	16.67
M = C_6H_4	1	0.78	3.4	3.4 [18]	0.20	0.04			5.00	25.00		
M = C_4H_2S	1	0.56	2.0	2.0 [19]	1.1	0.35			0.91	2.86		
(M_1–M_2)												
M_1 = C_6H_4												
M_2 = C_2	1.5	0.98	2.7	2.7 [20]	0.43				2.33			
M_2 = C_4	2.2	1.18	2.4			0.19	0.06	0.02		5.26	16.67	50.00
M_1 = C_4H_2S												
M_2 = C_2	1.5	0.77	1.9		1.5		0.32		0.67		3.13	
M_2 = C_4	2.2	0.97	1.9			0.66		0.94		1.52		1.06

respectively, are specified as $\beta \exp(-\eta)$ for single bonds and $\beta \exp \eta$ for double and triple bonds. (In other words, the single C–C bonds within rings and between rings, as well as double bonds within rings and triple bonds between rings, are assumed to have identical hopping integrals.) The carbon–carbon bonds within phenyl rings in all six-membered ring based oligomers are assumed to be equal to β and the single and triple C–C bonds between six-membered rings are specified as β_i and $\beta_i \exp(2\eta)$, respectively. All carbon-site energies are set to zero. For the thiophene system we also have to specify the hopping integral associated with S–C bond β_{S-C} and electron on-site energy at sulfur ϵ_S. The values of parameters used are: $\eta = 0.1333$ [15] for polyenes and $\eta = 0.1$ in all other cases; $\beta_{S-C} = 0.38\beta$ and $\epsilon_S = 0.25\beta$ [16]; $\beta_i = 0.92\beta$ and $\beta = -3.757$ eV [15] for all oligomers of focus. This choice of parameters reproduces the observed 1^1B_u transition frequencies in polyenes with three to seven double bonds [15] and agrees well with the experimental estimates of band gaps available for us, see Table 1.

For certain positions of E_F the definitions of decay constant and pre-exponential factor take especially simple form. Let $G^M_{\alpha_l,\alpha_l} G^M_{\alpha_r,\alpha_r} = 0$. This equation determines energies at which the system is capable to generate local states. As stated above we have excluded the case of local states and this implies that $|G^M_{\alpha_l,\alpha_r}(E_F)| < 1$ [12]. Then, from equations (6), (9) and (11) we have $g_0^{mol}(E_F) = 1$ and

$$\delta(E_F) = \ln|G^M_{\alpha_l,\alpha_r}|^{-2}. \quad (13)$$

Similar consideration for (M_1-M_2)-oligomers leads us to $g_0^{mol}(E_F) = |G^{M_2}_{\alpha_l,\alpha_r}|^{-1}$ and

$$\delta(E_F) = \ln|G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_{\alpha_l,\alpha_r}|^{-1}, \quad (14)$$

where E_F satisfies equations $G^{M_1}_{\alpha_l,\alpha_l} G^{M_1}_{\alpha_r,\alpha_r} = 0$ and $G^{M_2}_{\alpha_l,\alpha_l} G^{M_2}_{\alpha_r,\alpha_r} = 0$ and inequality $|G^{M_1}_{\alpha_l,\alpha_r} G^{M_2}_{\alpha_l,\alpha_r}| < 1$.

Importantly, in this particular case the pre-exponential factor is identical for all (M)-oligomers, i.e. it is oligomer independent that agrees with numerical findings [7]. For (M_1-M_2)-oligomers the value of $g_0^{mol}(E_F)$ is determined only by the electronic structure of the connecting, M_2, group, see examples in Table 1.

In the case of alternant, all carbon oligomers δ_{max} corresponds to the middle of HOMO-LUMO gap, i.e. $G^M_{\alpha_l,\alpha_l} = 0$ at $E = 0$. Therefore, δ_{max} can be found from equation (13) or equation (14). Expressed in terms of parameters of Hamiltonian (1) we obtain:

$$\delta_{max} = \begin{cases} 2\eta, & M = C_2H_2, \\ \ln(2\beta/\beta_i), & M = C_6H_4, \\ \ln(2\beta/\beta_i) + 2\eta, & M_1 = C_6H_4, M_2 = C_2, \\ \ln(2\beta/\beta_i) + 4\eta, & M_1 = C_6H_4, M_2 = C_4. \end{cases} \quad (15)$$

And for the rest of oligomers δ_{max} has to be found from equation (9).

As seen from equation (15), for polyenes the definition of δ_{max} coincides with the definition of half of the HOMO-LUMO gap in units of β, $\Delta_{HL}/(2\beta) = 2\eta$, if $\eta \ll 1$. (Note that in the derivation of equation (15) we did not use the smallness of the alternation parameter.) However, such a coincidence is misleading, if extended to other molecules. For instance, for the given model of poly-paraphenylene oligomers [12] $\Delta_{HL}/(2\beta) = \sqrt{2 + (1 - \beta_i/\beta)^2/4} - (1 + \beta_i/\beta)/2$. The latter equation bares little, if any, resemblance of the corresponding definition of δ_{max} in equation (15). This example is just an illustration of the fact that in general, there is no direct relationship between the decay constant, which is formed by all states of the molecule and the width of the energy gap.

The analytical results obtained above allows one to predict new physics. In particular, it can be shown that for special symmetries of monomers, e.g. such that $G^{M}_{\alpha_l,\alpha_r}$ as a function of energy can take zero value, equations (6) and (10) suggest an anomalously high resistance at certain energies, while near these energies the resistance is low. This unusual switching ability of molecular wires deserves separate discussion [21].

In conclusion, we have presented the exactly solvable model of single molecule conductance which relates the linear response current to the microscopic structure of the molecule placed between, e.g. the substrate and STM tip and similar metal–molecular heterojunctions. We have found analytical expression of the tunnel conductance for the wide class of linear molecules.

REFERENCES

1. Waldeck, D.H. and Beratan, D.N., *Science*, **261,** 1993, 576.
2. Joachim, C. and Gimzewski, J.K., *Chem. Phys. Lett.*, **265,** 1997, 353.
3. Bumm, L.A. *et al.*, *Science*, **271,** 1996, 1705.
4. Reed, M.A. *et al.*, *Science*, **278,** 1997, 252.
5. Datta, S. *et al.*, *Phys. Rev. Lett.*, **79,** 1997, 2530.
6. Samanta, M.P. *et al.*, *Phys. Rev.*, **B53,** 1996, R7626.
7. Magoga, M. and Joachim, C., *Phys. Rev.*, **B56,** 1997, 4722.
8. Mujica, V., Kemp, M. and Ratner, M.A., *J. Chem. Phys.*, **101,** 1994, 6856.
9. Datta, S. and Tian, W., *Phys. Rev.*, **B55,** 1997, R1914.
10. Heeger, A.J. *et al.*, *Rev. Mod. Phys.*, **60,** 1988, 781.
11. Landauer, R., *IBM J. Res. Develop.*, **1,** 1957, 233; *Philos. Mag.*, **21,** 1970, 683.
12. Onipko, A., Klymenko, Yu. and Malysheva, L., *J. Chem. Phys.*, **107,** 1997, 5032; 7331.
13. Malysheva, L. and Onipko, A., *Synthetic Metals*, **80,** 1996, 11; *J. Chem. Phys.*, **105,** 1996, 11032.
14. McConnell, H.M., *J. Chem. Phys.*, **35,** 1961, 508.
15. Kohler, B.E., *J. Chem. Phys.*, **93,** 1990, 5838.
16. Birnbaum, D., Kohler, B.E. and Spangler, C.W., *J. Chem. Phys.*, **94,** 1991, 1684.
17. Fink, J. and Leising, G., *Phys. Rev.*, **B34,** 1986, 5320.
18. Shacklette, L.W. *et al.*, *J. Chem. Phys.*, **73,** 1980, 4098.
19. Kaneto, K., Yoshino, K. and Inuishi, Y., *Solid State Commun.*, **46,** 1983, 389.
20. Roman, L.S. *et al.*, *J. Chem. Phys.*, **105,** 1996, 10614.
21. Onipko, A. and Klymenko, Y., *J. Phys. Chem. A*, **102,** 1988, 4246.