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Surface-specific resonances in the optical SHG spectrum at an adsorbate-covered semiconductor

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Abstract. The frequency dependence of second-harmonic generation (SHG) at an adsorbate-covered semiconductor surface is investigated. A one-dimensional model is proposed for the bulk carrier motion in the vicinity of the adsorbate. Numerical simulations were performed for the cases of carriers induced by charge transfer from strong donor- or acceptor-type adsorbates. The SHG spectra reveal strong resonant signal enhancement resulting from Rydberg-like states of the carrier-surface system.

1. Introduction

Optical second-harmonic generation (SHG) [1, 2] is one of the tools that enable a non-destructive diagnosis of clean and covered surfaces [3–8]. The centrosymmetry usually existing in a fluid or a condensed phase breaks at the surface and causes the appearance of a non-vanishing second-order non-linear susceptibility $\chi^{(2)}$. Simply by measuring the dependence of this parameter on the orientation of a surface with respect to the directions of polarization and propagation of the incident light one obtains information about the structure of the surface [5, 9].

Quite often in the discussion of SHG at an interface, the frequency dependence of $\chi^{(2)}$ is ignored. The latter is, however, of importance, since it contains detailed information about the non-linearity mechanisms responsible for SHG. Different processes in the adsorbate, at the covered surface and in the bulk near the surface, contribute to $\chi^{(2)}$ and become distinguishable by their frequency dependence. The model and advanced calculations of the non-linear response are also expected to be useful in clarifying the relations between the microscopic parameters and the observed SHG signals [10, 11]. In particular, the electronic structure of the surface can lead to resonant enhancement in the frequency dependence of the surface SHG signal [12, 13].

In this paper we consider a possible mechanism for optical SHG that can be attributed to specific surface states of a clean or covered surface. The spectral dependence of SHG is very complicated as it depends upon the energy spectrum of the compound adsorbate-surface system. We wish to discuss a particular cause for the origin of these dependencies and to propose a simplified model that describes one aspect of the typical behaviour of a semiconductor surface. Specifically we consider

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the charge transfer accompanying the adsorption that leads to the appearance of extra carriers near the surface. Unlike metals, the motion of these carriers in a semiconductor is not affected by the charge background and is the very reason for the non-linearity mechanism considered here. As a result Rydberg-like states of the carrier-surface system give rise to strong signal enhancement. It is of experimental interest in this context that the existence of such states for the somewhat different case of surface bands has recently been observed [12]. The relevance of the model to the real situation will be discussed in some detail in section 5.

2. The model

In a first approximation, a donor-type adsorbate primarily has the effect of supplying an electron to the conduction band of the semiconductor, while an acceptor-type adsorbate creates a hole in the valence band. The motion of the electron or the hole is described by a Schrödinger equation of the form

$$i\hbar\dot{\psi} = -\frac{\hbar^2}{2} \left[\frac{1}{m_x} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{m_y} \frac{\partial^2 \psi}{\partial y^2} + \frac{1}{m_z} \frac{\partial^2 \psi}{\partial z^2} \right] + U(x, y, z) \psi \quad (1)$$

with x, y and z denoting the principal axes of the mass tensor. The surface-specific non-linear susceptibility is obtained from the well known expression of third-order perturbation theory [1]

$$\chi^{(2)} = n_s \sum_{\{j,k\},\{p,q\}} \frac{\mu_{0,j} \mu_{j,k} \mu_{k,0}}{E_0 + E_0^{(f)} - E_j - E_p^{(f)} E_0 + E_0^{(f)} - E_k - E_q^{(f)}} \mu_{k,0} \quad (2)$$

where $\mu_{i,j}$ are the dipole matrix elements and n_s is the adsorbate surface density. The summation in (2) extends over all accessible quantum states of the system with energies E_j ($j = 0, 1, 2, \dots$) and of the field $E_p^{(f)} \doteq N_1 \hbar \omega + N_2 2 \hbar \omega$. The state of the field $E_0^{(f)} = N \hbar \omega$ corresponds to the initial presence of N photons of the pumping field at the frequency ω . Here we ignore any contribution to SHG from internal degrees of freedom of the adsorbed molecules that arises just because of the effect of orientation [14].

A high anisotropy of the mass tensor, e.g. $m_x \ll m_y, m_z$, is typical of semiconductors. This allows us to reduce the calculation of $\chi^{(2)}$ to a one-dimensional problem by calculating the eigenstates of the Hamiltonian

$$-\frac{\hbar^2}{2m_x} \frac{d^2 \psi_j}{dx^2} + U(x) \psi_j = E_j \psi_j(x) \quad (3)$$

with x being the direction perpendicular to the surface. For a semiconductor surface the interaction between substrate and adsorbate should be well localized and the shielding effect by free carriers in the bulk plays no role. Hence the carrier in the bulk is subject to the action of an almost Coulomb-like field due to the adsorbate core. The potential energy of a carrier is thus of the form

$$U(x) = \begin{cases} -ee_c/x + 4\pi en_s x + U_c(x) & x > 0 \\ \infty & x < 0 \end{cases} \quad (4)$$

where e and e_c are the charges of the carrier and the centre, respectively. We assume that the carriers only exist in the solid and take into account the effect of polarization of the adsorbate core by the term U_c . The collective behaviour of the electrons from different adsorbate sites is modelled by the term $4\pi en_s x$ in (4). Such an expression clearly forms only a very crude model for this collective motion. An improved approximation is possible by using the self-consistent field that allows for screening. The potential at large distances then takes the form

$$U(x \gg 0) = 4\pi en_s \int_0^x \int_{x'}^{\infty} |\psi(x'')|^2 dx'' dx'. \quad (5)$$

This expression follows by an integration of Poisson's equation $\nabla^2 U = 4\pi\sigma$ in the one-dimensional case, using the charge density $\sigma = n_s e |\psi(x)|^2$. Equation (5) then replaces the term linear in x in (4). However, we will not consider this modification in the numerical calculations and thereby restrict ourselves to the case of low adsorbate coverage.

Without the second and third terms in the potential of (4) a solution of (3) will lead to the one-dimensional Rydberg spectrum $E_n = -R^*/n^2$. The Rydberg constant is scaled by a factor m_x/m_e and the typical size of the electron cloud is m_e/m_x times larger than the Bohr radius a_0 . For the example of a typical effective mass m_x of order $0.2m_{y,z}$, it implies that the three-dimensional wavefunctions are significantly stretched along the x direction. The latter justifies the one-dimensional approach to the problem used here. The effect of this mass difference becomes even more significant for the third-order term $\chi^{(2)}$ which scales as $(m_x/m_e)^3$.

3. Method of calculation

Even with all the simplifications already introduced, the actual numerical evaluation of $\chi^{(2)}$ by expression (2) and with the energies and wavefunctions of eigenstates calculated according to (3) remains difficult. The main problem arises from the influence of the continuous and/or very dense spectrum near the edge of the band gap, which corresponds to an infinite or nearly infinite motion of the carrier and thus possesses very large values of the dipole moment. However, the total contribution of these states effectively cancels in the sum in (2).

In order to avoid this difficulty we implement a Green function method and use an approximate expression for the Green functions that involves only a limited number of wavefunctions, instead of the infinite set of eigenstates. We express the susceptibility in (2) as

$$\begin{aligned} \chi^{(2)}/n_s = & \text{Tr}\{\hat{\rho}\hat{\mu}\hat{G}(\hbar\omega)\hat{\mu}\hat{G}(2\hbar\omega)\hat{\mu}\} + \text{Tr}\{\hat{\rho}\hat{\mu}\hat{G}(-2\hbar\omega)\hat{\mu}\hat{G}(-\hbar\omega)\hat{\mu}\} \\ & + \text{Tr}\{\hat{\rho}\hat{\mu}\hat{G}(\hbar\omega)\hat{\mu}\hat{G}(-\hbar\omega)\hat{\mu}\} \end{aligned} \quad (6)$$

where $\hat{\rho}$ is the density matrix of the system and the Green function for a given value of the energy

$$\hat{G}(E) = \sum_k \frac{|\psi(E_k)\rangle\langle\psi(E_k)|}{E - E_k} \quad (7)$$

is represented in terms of the the eigenvalue spectrum $\{E_k\}$. We denote a Green function with argument $E_i + p\hbar\omega$ by $\hat{G}(p\hbar\omega)$, E_i being the energy of the initial state. In the framework of this approach possible relaxation processes, like spontaneous emission, collisional relaxation etc, can be treated by adding an imaginary part γ_k to the denominator of the Green function in (7). The calculation of $\chi^{(2)}$ based on the form of (7) for the Green function is equivalent to (2) and requires considerable numerical effort because regions with a very dense or even continuous energy spectrum give significant contributions. The following approximation to the Green function leads to a much more convenient computational procedure. Whenever the wavefunction $\psi(x; E)$ is analytical in E , equation (7) can be rewritten in the form

$$\hat{G}(E) = |\psi(E)\rangle\langle\psi(E)| \sum_k \frac{1}{E - E_k}. \quad (8)$$

Otherwise, if the wavefunction is not analytical, we should subtract a contribution obtained from circumventing the set of singularities of $\psi(E)$ in the complex plane. One can argue, however, that the effect of these singularities is small. Indeed, the wavefunction $\psi(E; x)$ enters the formula for $\chi^{(2)}$ only via the matrix elements $\langle\psi(E; x)|x|\psi(E'; x)\rangle$. Whenever these values are smooth functions of E and E' the wavefunctions in (7) can be written in front of the summation sign for the following reasons: the wavefunction as a function of the coordinates never tends to infinity at the regular points of the potential in the Schrödinger equation. Hence, $\psi(x; E)$ as a function of energy has no poles, and the only possible singularities are the branching points. At a given value of x these branching points are then the energies at which x becomes a turning point of the motion. In the semiclassical approximation the wavefunction has a $[E - U(x)]^{-1/4}$ dependence on the energy. This dependence is smooth enough to justify the step leading to (8). The substitution of (8) into (6) then gives the final expression for the non-linear susceptibility $\chi^{(2)}$.

4. Results

The wavefunctions required by (7) and (8) were generated by a numerical solution of (3) for arbitrary E using the condition $\psi(x) = 0$ far inside the bulk. Since $\psi(0) = 0$ for any of the eigenvalues E_k , one may use the relation

$$\frac{\partial \ln \psi(E, x=0)}{\partial E} = \sum_k \frac{1}{E - E_k} \quad (9)$$

to replace the corresponding term in (8). Note that both sides of (9) have identical poles and residues and thus represent the same analytical function under very general conditions. The Green function is then used to determine $\chi^{(2)}$ from (6). By solving (3) for complex energy values, this method is easily extended to also describe the irreversible decay of levels. The results of a calculation of $\chi^{(2)}$ for pumping in the visible region of the spectrum are represented in figures 1 and 2. In these calculations we performed numerical solutions of (3) and (4) for parameters chosen to represent the cases of light carriers in silicon and germanium.

The most obvious features seen in the calculated spectra are the pronounced resonances. The positions of these resonances coincide with transition frequencies

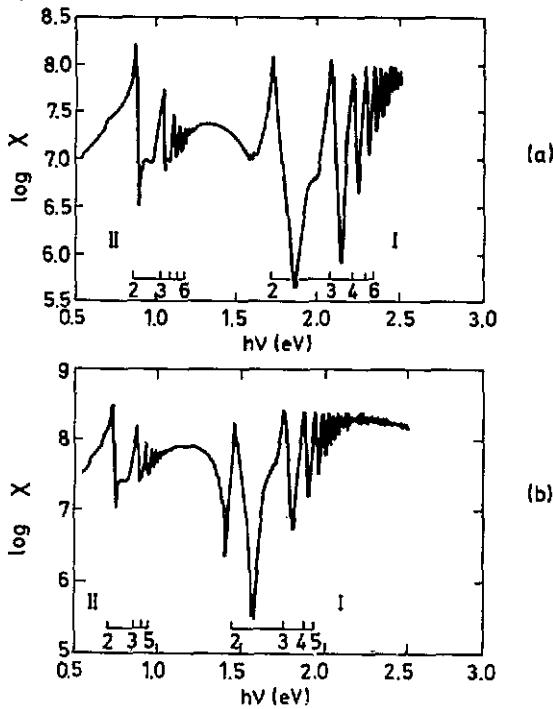


Figure 1. Calculated spectral dependence of the non-linear susceptibility $\chi^{(2)}$ (in atomic units) for a Si/adsorbate model system. The carrier lifetime was set equal to 10^{-14} s. (a) Light electrons (the adsorbate is of donor type): $m_e^* = 0.2 m_e$; eigenenergies $E_n = -2.36, -0.625, -0.270, -0.133, -0.059, -0.0096$ eV ($n = 1, 2, 3, \dots$). Note the two series of Rydberg resonances $1 \rightarrow n$ for the first (I) and second (II) harmonic of the pump laser. The numbers on the scales denote the principal quantum number of the final state. (b) Light holes (the adsorbate of acceptor type): $m_h^* = 0.16 m_e$; $E_n = -1.96, -0.506, -0.212, -0.094, -0.029$ eV. Besides the Rydberg series small oscillations occur on the high-frequency side. They correspond to cooperative carrier motions.

in the bound-carrier level system and with half of these values. This fact is in complete agreement with (2) according to which the resonant denominators tend to zero whenever the energies of either the quanta of the first or of the second harmonic coincide with a transition frequency. The small modification of the Coulomb potential due to the influence of the atomic core polarization was taken into account by a model core potential

$$U_c(x) = \frac{\mu}{(x+a)^2} \quad (10)$$

where μ is an effective stationary dipole moment of the core, and a is a specific distance from the surface at which the dipole is located. Both values are treated here as essentially free parameters. It was found that the core potential can shift the positions of the resonances. A strong perturbation of the Coulomb potential by the core affects the potential even at large distances and drastically changes the frequency dependence.

Apart from the observed strong resonances the absolute magnitude of the calculated non-linear susceptibility is also of interest. Typical values for $\chi^{(2)}$ are as

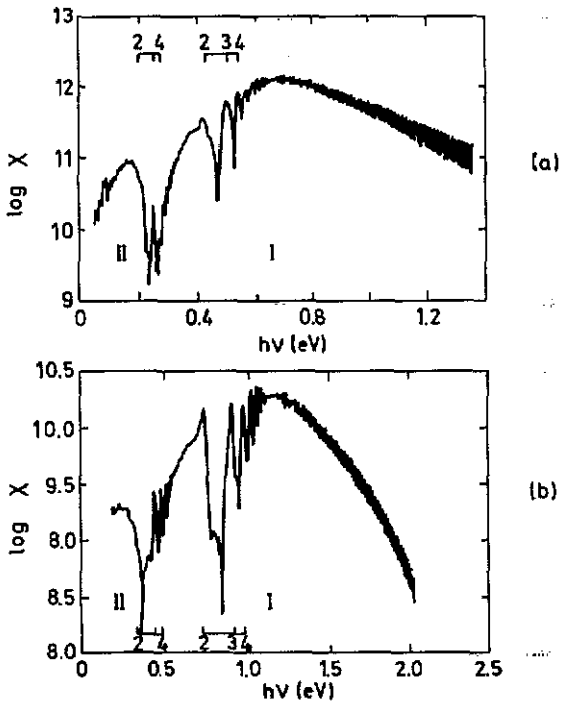


Figure 2. Calculated $\chi^{(2)}$ spectra for a Ge-adsorbate system. Carrier lifetime is 10^{-14} s. (a) Light holes; $m_h^* = 0.044 m_e$; $E_n = -0.548, -0.137, -0.047, -0.0065$ eV. The effect of cooperative carrier motion is seen at the blue side of the spectrum. Irregularities at small frequencies are due to computational inaccuracy near $\omega = 0$. (b) Light electrons; $m_e^* = 0.08 m_e$; $E_n = -0.991, -0.249, -0.092, -0.023$ eV. A pure case of an SHG spectrum resulting from Rydberg states of the surface carrier can be seen. The small carrier masses are responsible for the larger amplitudes of the oscillations and hence for large values of $\chi^{(2)}$ in comparison with the Si case.

large as 10^8 au for the case of silicon (figure 1) and 10^{11} au for Ge (figure 2). In both cases a linewidth corresponding to a relaxation time of 10^{-14} s is assumed. In more conventional units the surface susceptibility is then of the order of 3×10^{-19} and $3 \times 10^{-16} \text{ m}^2 \text{ V}^{-1}$, respectively, if one assumes a surface adsorbate density $n_s = 10^{18} \text{ m}^{-2}$. For comparison average values of $\chi^{(2)} \sim 2 \times 10^{-21} \text{ m}^2 \text{ V}^{-1}$ for Si(111)7 \times 7 and Si(111)1 \times 1-As have been reported recently [13]. The existence of resonances as well as the large dipole moments resulting from the small effective mass of the carriers in semiconductors are thus the two main reasons for the large size of the effect.

The results of the calculations are presented here for the case of low surface coverage, i.e. all adsorbed species contribute independently to the process. A high coverage of adsorbates and a high intensity of the pumping field may result in a cooperative behaviour of the carriers. This manifests itself on the short-wavelength range of the spectrum. The quantum states involved in this range are located above the energy threshold for the free motion of a single carrier.

5. Discussion

The present model describes a possible mechanism for the optical non-linearity of

an adsorbate-covered semiconductor as a result of specific non-linear motions of the carriers at the surface. We first discuss the chemical nature of the surface states, corresponding to this motion. We emphasize that even a clean semiconductor surface possesses specific surface electronic states [15, 16], the Tamm states [17], which are formed by the unshared electrons in unsaturated chemical bonds at surface-located atoms. On the reconstructed surface these states form an aggregation by chemical bonding among the surface atoms. Some atoms change their location at the surface and form strong chemical bonds as a result. For a silicon surface this results in the appearance of the 2×1 or 7×7 structures [18–24] in which some of the surface atoms still have unsaturated bonds. Surface reconstruction also affects the energies of these surface states by causing small energy shifts (~ 0.1 eV). Chemically most active is the partially occupied state S_1 that pins the Fermi level of a semiconductor to the vicinity of the centre of the band gap. In the simplest picture this S_1 state corresponds to a valence electron in an unsaturated surface-atom bond and is responsible for adsorbate bonding [25]. It is also known that the coupling between the S_1 states of different surface cells leads to the formation of surface bands for the motion of an electron or a hole along the surface. These additional degrees of freedom lift the degeneracy of the surface states that exists when each valence electron in the dangling orbital is assumed to exclusively occupy its own cell.

The effect of the free surface is not treated by the model discussed in this paper, but it will be underlying the contribution to $\chi^{(2)}$ originating from an adsorbate. At a free surface the existence of the single-occupied surface state also leads to a specific non-linear carrier dynamics under the action of a time-dependent perturbation by an optical field. The fact that both positive and negative carriers now participate simultaneously in the SHG process complicates any analytical description of this process. No attempt is made here to treat the free-surface contribution to SHG for at least two other reasons: first, other than in the case of strong donor–acceptor-type adsorbates, even an approximate explicit expression for this potential is difficult to obtain. Apart from the Coulomb potential the exchange-correlation interaction is also of importance, as it is the very reason why the carriers remain near the surface and form a dangling bond in the absence of optical pumping. Second, no experimental information on the frequency dependence of $\chi^{(2)}$ is presently available from SHG studies of a free Si surface [9, 26].

In the presence of an adsorbate the surface states undergo changes in energy and in extreme cases become of a rather simple nature. In the extreme case of a strong donor-type adsorbate an electron is supplied to the conduction band. In a similar way an acceptor-type adsorbate creates a hole in the valence band. In both extremes there is only one carrier that moves in the Coulomb potential of the surface-pinned centre of opposite charge. This fact allows the one-particle approximation to be introduced into the model. Changes in the surface-state energies due to surface reconstruction and surface bond formation are small compared with the changes induced by the adsorption, and we ignore the former complicated aggregation structure at the surface when considering the chemisorption process and its influence on the frequency dependence of the non-linear susceptibility $\chi^{(2)}$. The difference between this oversimplified 1×1 structure and the other more complicated aggregations (e.g. the 7×7 structure) is expected to manifest itself primarily in the angular dependence of the SHG signal.

The one-electron eigenstate spectrum of the surface states is then responsible for the frequency dependence of the second-order susceptibility $\chi^{(2)}$. This spec-

trum is determined by the one-electron (or one-hole) potential which is specific for both the adsorbate and the surface and results from both the Coulomb and exchange/correlation interactions. In this paper we have considered simple approximate forms for these potentials. In the extreme case of a strong donor or acceptor adsorbed at the surface, the Coulomb potential gives the main contribution to the one-particle potential, and the exchange potential is of no importance. The small influence of the adsorbate core can be taken into account by means of an effective polarization potential $U_c \sim x^{-2}$. It results in a small shift of the SHG spectra as compared with the pure Coulomb case. We also take advantage of the fact that the motion of adsorbate electrons in the bulk is different from the motion of an electron in free space. The high anisotropy of the carrier mass tensor typical of the bulk of semiconductors results in a considerable simplification and, in particular, to a one-dimensional description of the carrier motion.

A recent investigation of the CaF_2 -Si(111) interface by three wave-mixing techniques has shown the appearance of an excitonic resonance below the surface conduction band [12]. It must be admitted that the specific system chosen does not fall into the category of a strong donor-acceptor that allowed us to consider the motion of a single carrier only. However, the experimental observation supports the basic assumption of our model that adsorption can cause the appearance of specific surface electronic states that strongly affect the non-linearity behaviour of the surface. The description of such two-dimensional motions requires a more refined examination as the motion is determined to great extent by details of the surface region. On the contrary the case envisaged in our model is relevant when the carrier motion is primarily in the direction perpendicular to the surface, leading to much simpler forms of the typical potentials.

An important and well known general advantage of the SHG method in the experimental investigation of surface states is apparent in contrast to linear absorption spectroscopy or electron energy loss spectroscopy (EELS) where transitions among the surface states have to be detected against the background of the analogous bulk processes. The SHG spectra are to a much lesser extent aggravated by this background. This is because: (i) only the processes at the surface where the central symmetry is broken contribute to the SHG spectra; and (ii) the spectra obtained in our model calculations have resonances at frequencies of the order of half of the energy band gap and thus are not influenced by the bulk one-photon absorption.

It is expected that the resonances predicted by the mechanism underlying the present model will certainly be less sharp in an experimental observation if a comparison is made with the structure seen in our numerical calculations. One reason for this is surface reconstruction. Even though the electronic surface states have rather large spatial dimensions, they are, nevertheless, affected by the surroundings of the adsorbed atom. This affects the ground-state energy of the carrier and causes a shift of the spectral dependence of $\chi^{(2)}$. Averaging the shifts over the adsorbate sites causes inhomogeneous broadening of the spectra. Another reason is that in reality the motions are not one-dimensional. Compared with the one-dimensional Coulomb case the energy spectrum then becomes much more complicated and is perturbed by other degrees of freedom. As a consequence the periodicity of the carrier motion is destroyed, i.e. the carrier seldom returns to the initial state while the corresponding classical problem shows chaotic motion. By introducing a finite effective lifetime it should be possible to treat this situation in the framework of the present model. Thus in both cases a broadening of the resonances in the frequency dependence of $\chi^{(2)}$

will be the main result.

The charge carrier motions discussed here affect the electron energy loss spectra and the linear absorption spectra. But a direct comparison of such data with the results of the $\chi^{(2)}$ spectroscopy seems to be difficult. Nevertheless, in contrast to EELS, the optical second-harmonic spectroscopy allows, at least in principle, the resonance structure of the surface states to be resolved if one can distinguish between the contributions due to the homogeneous and inhomogeneous broadening of the spectral lines.

The results obtained in this paper are valid primarily for the extreme cases of either a strong donor or a strong acceptor, e.g. an alkali or halogen atom, respectively, adsorbed on a silicon surface. In the case of a moderately strong adsorbate interaction the calculations require the true quantum-chemical two-particle multi-dimensional potentials. In this case the spectral dependencies tend to be complicated even in the absence of inhomogeneous broadening due to surface reconstruction. The optimal situation for the observation of the resonant structure in the $\chi^{(2)}$ spectra seems to be realized for a semiconductor surface with a low coverage of a strong donor- or acceptor-type adsorbate. Then each adsorbed atom only occupies a certain fixed site of the reconstructed surface cell. The inhomogeneous broadening of the spectral line is absent in this case and the $\chi^{(2)}$ spectra for all types of strong donors or acceptors are expected to have forms similar to the ones shown in figures 1 and 2.

In summary, the present analysis indicates the existence of Rydberg-like structures in the SHG spectra of semiconductor surfaces covered by strong donor/acceptor adsorbates. These spectra result from the essentially one-dimensional motions of the carriers in a semiconductor with strong mass anisotropy and reflect the largely ionic character of the adsorbate binding.

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