# *Ab Initio* Calculations of Anharmonicity of the C-H stretch mode in HCN and GaAs.

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## Abstract

The anharmonicities of the C-H stretch modes in HCN and the passivated C acceptor in GaAs are investigated using *ab initio* local density functional cluster theory. The effective mass parameter, $\chi$, for the C-H stretch mode is shown to be less than unity in HCN, and greater than unity for the GaAs case. The calculated anharmonic parameter for the first defect is found to be 106 cm$^{-1}$ and is in very good agreement with experiment. For the second defect, the anharmonicity is about 50% larger in agreement with empirical estimates. The frequencies of the fundamental transitions in both systems are shown to be very sensitive to the C-H length. This limits the accuracy of theoretical investigations of these high frequency H modes. Finally, the effects of electrical anharmonicity are considered and it is shown that they reduce the intensity of the overtone in the C-H complex in GaAs by about 70%.

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## I. INTRODUCTION

Anharmonicity has several important consequences for atomic vibrations in solids. Besides the usual implications such as thermal expansion and lattice thermal resistance, it contributes to the decay of local vibrational modes (LVM's) of defects and leads to a breadth in their infra-red absorption lines. It also breaks the selection rule preventing an electrical dipole transition between states of the same parity, and this allows overtones of fundamental lattice transitions to be observed. The effects of anharmonicity are notoriously difficult to calculate as they involve high-order derivatives in the potential energy. In principle these could be derived as the energy for the ground state, $E$, can be computed, within the Born-Oppenheimer approximation, for any arrangement of nuclei. It is straight-forward to determine the minima of $E$, and hence the structure of the solid and its defects, as well as the second derivatives of $E$ [1–3] which can then be used to evaluate the lattice frequencies and LVM's. The third or higher order derivatives of $E$ could be found in the same way, but it is not clear that expansions to third or even fourth order are really sufficient to describe anharmonic effects although it is almost universal practice to do so. This is an important consideration which we shall dwell upon later.

The anharmonic effects on the LVM's due to light impurities, and especially H, in semiconductors are particularly large. This is because the amplitude of the vibration of the H atom, $\approx 0.2$ Å, implies that H explores a region that is outside the harmonic regime. Several features due to anharmonicity in the LVM's of H defects have been observed [4–6] and this has given an impetus to investigate anharmonic effects from a theoretical viewpoint. Previous investigations of mechanical anharmonic effects have usually been carried out assuming either a potential involving cubic and quartic terms in the displacement of H from its equilibrium position [4], or a Morse potential [7,6]. There is, in addition, another form of anharmonicity that has been been often neglected [8]: that of electrical anharmonicity. This is where the dipole moment varies non-linearly in the normal coordinate. This by itself would induce a transition between the ground and second excited state of a harmonic oscillator. In practice both forms of anharmonicity are always present and there is a need to quantify each type.

The aims of this paper are to explore the anharmonicities of the C-H stretch mode when C is bonded to N, as in the prussic acid molecule HCN, and when C is a substitutional defect in GaAs. In the latter case the structure of the defect is believed to be that illustrated in Fig. 1. There have been classical observations of the overtone to the C-H stretch mode in HCN [7] whereas in the second example the anomalous isotopic shifts observed in the LVM's have been explained in terms of anharmonic effects [5].

It is usual to write the frequency, $\nu$, of the H stretch mode of H-C-X as [9]:

$$\nu^2 = k(1/M_H + 1/\chi M_C). \tag{1}$$

Here $k$ is the force constant of the oscillator and $\chi$ is an effective mass parameter which depends on the coupling of C with X and is only weakly dependent on $M_H$. For a diatomic species, HC, the term $\chi$ is unity. When X is some atom, or the remaining crystal lattice, bonded to C, it is often argued that $\chi$ is greater than unity as the motion of C is constrained by the lattice and this increases the effective mass of C. However, this argument is not always correct. Indeed, it might equally be argued that if C is strongly bonded to X, then the slight motion of C involved in the H stretch mode costs extra energy as the C-X bond is compressed. Thus the H-stretch frequency would increase over the value determined by the constant $k$ and the reduced mass alone, and this requires $\chi$ to be less than unity. We shall show below that this occurs in the prussic acid molecule where the C-N bond is very strong. For the C-H stretch mode in GaAs, Davidson et al [5] fitted Eq.(1) to the frequencies of four isotopic combinations (H, D, $^{12}$C, $^{13}$C) that they had observed, and found $\chi$ to be less than unity. In this case there is no strong bond that is compressed when C moves — only a bend in the three C-Ga bonds. A value of $\chi$ less than unity is then unphysical. The suggestion was then made that if anharmonic effects are included then the the harmonic frequencies in Eq. (1) are related to the observed fundamental transition frequencies, $\omega$, through an anharmonic parameter, $B$, given by:

$$\omega = \nu - B/M. \tag{2}$$

Using the observed values of the C-H stretch frequency for two isotopes of C and H (Table 1), and taking $M$ to be the mass of the H atom, $B$ and $\chi$ were found to be 176 amu cm$^{-1}$ and 1.1 respectively [5]. The implication is then that anharmonic effects are particularly large and the anomalous isotope shifts are to be understood as arising from these. However, no overtone to the fundamental transition was reported. Now, an overtone has been observed for the C-H vibration of the HCN molecule which has an anharmonicity parameter of 102 amu cm$^{-1}$ [7]. This is much smaller than $B$ for the stretch mode in GaAs. The anharmonicity parameter quoted above for HCN is related to the difference between the overtone and twice the fundamental frequency but is equal to $B$ in low order perturbation theory, i.e. when the quartic terms are treated in first order and the cubic terms in second order. These experimental results raise the question as to why the anharmonicity is so large for C-H in GaAs and yet the intensity of the overtone seems to be so low. One of the motivations of this paper is to investigate these anharmonic effects and the relative strengths of the overtone and fundamental transitions.

In Sec. II we describe previous investigations of the C-H defect in GaAs. We have recently reconsidered the calculation of the LVM's of this defect using an improved numerical method over our previous investigations and this has given a better agreement with the observed low lying LVM's. The modified procedure, however, worsened the agreement for the C-H stretch mode and this is a consequence of anharmonicity. In Sec. III we describe the changes to the theory and elaborate on the methods used here to investigate anharmonicity. This theory is then applied to HCN in Sec. IV and to the C-H defect in GaAs in Sec. V. In Sec. VI the effects of electrical anharmonicity are considered. Finally, our conclusions are given in Sec. VII.

## II. PREVIOUS STUDIES OF THE C-H COMPLEX IN GAAS

Carbon is known to substitute for As in GaAs and thus behave as a shallow acceptor. Clerjaud et al [10] found a C-H stretch frequency at 2635 cm$^{-1}$ in liquid encapsulated Czochralski grown GaAs contaminated by C and H. This was assigned to the C-H stretch mode through the observation of a shift of $\approx$ 7 cm$^{-1}$ from $^{13}$C-H. The magnitude of this shift is consistent with H being bonded to a mass approximately 12 amu. Confirmation for the presence of H in the defect was given by the observation of the C-D line at 1969 $cm^{-1}$ [11]. The approximate $\sqrt{2}$ reduction in frequency is indicative of a H stretch mode. Uniaxial stress measurements [12] established that the defect has trigonal symmetry and hence the H atom is located either close to a bond centered or anti-bonding site to C along <111>. Our previous *ab initio* cluster calculations [13,14] concluded that H was located near a bond centered site (Fig. 1) with a very short C-H length of 1.12 Å. The reorientation energy for H around the four <111> axes was calculated to be 0.67 eV – close to the observed value of 0.5 eV [12]. This theory gave the C-H stretch mode to be 2605 $cm^{-1}$ and in good agreement with the observed value. The $E^-$-mode, which involves a movement of H perpendicular to the $C_{3v}$ axis, and out of phase with C, was placed around 715 $cm^{-1}$. The C-$A_1$ and $E^+$ modes, which involve motion of H in phase with C in respective directions parallel and perpendicular to the C-H bond, were calculated to lie at 413 and 380 $cm^{-1}$ respectively.

Infra-red spectroscopy on GaAs containing high concentrations of C and H grown by molecular beam epitaxial and chemical vapor deposition methods found further modes at 453 (X) and 563 $cm^{-1}$ (Y) [15]. Both were subsequently shown to be due to the C-H defect as they exhibited shifts with C and H isotopes. A Raman scattering experiment [16,17] assigned the 453 $cm^{-1}$ to the C-$A_1$ mode. Y is now believed to be the $E^+$ mode [5]. The $E^-$ mode was not observed in these early experiments. However, in deuterated samples, the $E^-$ mode was detected at 637 $cm^{-1}$. This must imply that the unobserved H-$E^-$ mode lies above 637 $cm^{-1}$ and a simple force constant model [5] predicted it to lie at 745.2 $cm^{-1}$. The failure of the infra-red experiments to locate the H-$E^-$ mode was explained by the *ab initio* theory as the consequence of a small transition dipole moment. Very recently this mode has been detected at 739 $cm^{-1}$ by Raman scattering experiments [25].

The $E^{\pm}$ assignments were made more difficult not only because of the initial failure to observe the H-$E^-$-mode, but also because the interaction between them invalidates Eq. (1). The modes attempt to cross each other when D replaces H. Thus although the displacement of H dominates the $E^-$ mode, the displacement of C becomes increasingly important for the deuterated case. The opposite is true for the $E^+$ mode [5].

The C-H defect is the only H-passivated shallow impurity for which all the LVM's have been detected. This wealth of experimental data and the discrepancies with the theoretical calculations prompted us to reconsider the problem using a much larger basis set to describe the wavefunctions [25]. Details of these changes are given below. The new basis set gives the C-H and H-Ga bond lengths to be 1.126 and 2.253 Å respectively and the calculated modes are given in Table I. A discussion of these modes is given in [25]. The low-lying modes are now in much better agreement with experiment, but the C-H stretch mode and $E^-$ are placed much higher than before. This, we shall show below is due to the effect of anharmonicity.

A recent plane wave supercell calculation [18] has also found the bond-centered defect to be the most stable. The C-H and C-Ga lengths were found to be 1.2 and 2.0 Å respectively and the C-H stretch and $E^-$ frequencies lie at 2781 and 724 $cm^{-1}$. There is no direct experimental evidence for the location of H, but the prevailing viewpoint is that acceptors are passivated with H in this configuration and donors are passivated with H at an anti-bonding site to either the impurity, as in $Si_{Ga}$ [29], or to one of its neighbors, e.g. P in Si [19,20]. In some cases, channelling experiments show directly the location of H, e.g. the B acceptor in Si [21,22]. Indirect evidence for the bond centered location is that the magnitude of the lattice contraction caused when the C-H complex dissociates, and H is expelled from the lattice, agrees quantitatively with the structure predicted by the bond centered geometry [23].

## III. METHOD

### A. *Ab initio* Theory

The calculations used here are *ab initio* local density functional pseudopotential ones carried out on large H-terminated clusters [2]. The electronic wavefunctions are expanded in $s$ and $p$ Gaussian orbitals centered at nuclei as well as at bond centers.

In the case of the C-H complex in GaAs, eight Gaussian functions of different exponents were used on C and the surrounding four Ga atoms and two on H. The wavefunction basis on all the other atoms consisted of a linear combinations of these Gaussian functions. The charge density was fitted to eight Gaussian functions on C, Ga and As and three on each H atom. In addition bond centered Gaussian orbitals and fitting functions for the charge density were placed at every bond except those with H. This is a substantially larger basis than we used in our first calculation [13]. In that work four Gaussian orbitals and five fitting functions were placed on C, Ga and As sites. In order to be certain that this basis set is sufficiently large, we carried out further runs with four Gaussian orbitals and fitting functions on the central H atom. The C-H bond length was unchanged and the C-H stretch frequency changed insignificantly from the results given in Table I. The same sized basis has also been used for C defects, including the C-H complex, in AlAs [24,26]. Table I shows the calculated and experimental modes [27]. In both GaAs and AlAs the C-H stretch modes are too high in frequency but the other modes are in good agreement.

For the HCN molecule, eight Gaussian $s$ and $p$ orbitals were placed at the N site to describe the wavefunctions and eight fitting functions were used for the charge density basis. Six functions were used for C, and the H basis was the same as the C-H complex in GaAs. Bond centered functions were placed in every bond.

Norm-conserving pseudopotentials of ref. [28] were used and removed the need to include core electrons. The self-consistent energy $E$ and the force on each atom were calculated and the atoms moved by a conjugate gradient algorithm until equilibrium was attained. The second derivatives of $E$ between selected atoms were evaluated in the way described previously [2], i.e. each atom was displaced by 0.09 au from equilibrium and the force on all the selected atoms evaluated. Then the atom was displaced by -0.09 au and the forces re-evaluated. The second derivatives on the displaced atom and the others could then be found from the two-sided difference formula for the second derivative. It is important to realize that this prescription does not lead to *harmonic* force constants as there are quartic and higher order correction terms in these estimates of the second derivatives. We refer to the frequencies arising from these force constants as *quasi-harmonic*. If all the second derivatives $E_{ij}$ are evaluated then the dynamical matrix can be found directly as

$$E_{i,j}/\sqrt{M_i M_j}.$$

Here $M_i$ is the mass of the $i^{th}$ atom. All the entries to the dynamical matrix for HCN were found from the *ab initio* program. For the C-H defect in GaAs, only the derivatives between C, H and the four Ga neighbors were evaluated. The contributions to the dynamical matrix from all the other derivatives are taken from a Musgrave-Pople potential found earlier [29]. This potential was found from a fit to the double derivatives evaluated from a cluster representing bulk material and gave the TO mode at $\Gamma$ to within 20 $\text{cm}^{-1}$ of the experimental mode.

If the H stretch mode is decoupled from all other modes, it is only necessary to consider those energy derivatives between C and H along the bond direction. Suppose these derivatives are $E_{i,j}$ where $i = C$ or $H$. Then the quasi-harmonic C-H frequencies, $\nu$, are the eigenvalues of the dynamical matrix and are given by:

$$\nu^2 = \frac{E_{H,H}}{M_H} - \frac{E_{C,H}^2}{M_H(E_{C,C} - M_C\nu^2)} \tag{3}$$

Using,

$$\nu^2 = E_{H,H}(1/M_H + 1/\chi M_C) \tag{4}$$

allows us to write $\chi$ as:

$$\chi = \left(\frac{E_{H,H}}{E_{C,H}}\right)^2 \left(1 - \frac{E_{C,C}}{E_{H,H}}\frac{M_H}{M_C} + \frac{M_H}{\chi M_C}\right). \tag{5}$$

We shall use Eq. (5) below to determine $\chi$ for HCN and the C-H defect in GaAs.

We note $\chi$ is only weakly dependent on $M_H$ if the second and third terms in the sum are small. This is only true when

$$E_{C,C}/E_{H,H} << M_C/M_H.$$

If this were not true and $E_{C,C}$ is large, such as occurs when the C-X bond is strong, then $\chi$ can be less than unity as we shall see below. If the C atom was decoupled from the rest of the lattice then the translational symmetry of the resulting diatomic CH molecule would require:

$$E_{H,H} = E_{C,C} = -E_{C,H}. \tag{6}$$

These inserted into Eq. (5) yield $\chi = 1$ and

$$\nu^2 = E_{H,H}(1/M_H + 1/M_C)$$

as expected.

### B. The Anharmonic Oscillator

So far, we have treated the anharmonic terms in an approximate way by using a finite difference method to evaluate $E_{i,j}$. We now treat them more systematically. When the H atom moves in an anharmonic manner, the coupling between motion along and perpendicular to the C-H axis should be considered. This however, turns the problem into a three dimensional one which is difficult to solve. However, since the C-H stretch mode occurs at a much higher frequency than the bend mode in either HCN or CH in GaAs, it is reasonable to neglect the coupling between the two types of motion. The problem then reduces to motion along the C-H bond.

We evaluated the energy $E$ for displacements $x$ away from the equilibrium values. $E$ was then fitted to the polynomial expression:

$$E = E_0 + \sum_{i=2}^{m} a_i x^i. \tag{7}$$

In order for the oscillator wavefunctions to decay to zero at infinity, we require $m$ to be even and $a_m > 0$. We used values of $m$ up to 8. A standard least squares fit to the data with Chebyshev polynomials was used to extract the power series in Eq. (7).

One problem in the determination of the anharmonic frequencies is the choice of the oscillator mass $M$. If X was absent, then $M$ must be the reduced mass of C-H. However, in the presence of X it is not clear whether $M$ should include $\chi$. In practice the effect of $\chi$ is rather small and leads to shifts of about 30 $\mathrm{cm}^{-1}$ in the fundamental frequency. In the following, we have included $\chi$ in the expression for the oscillator mass:

$$M = M_H M_C \chi / (\chi M_C + M_H). \tag{8}$$

This means that our calculated values of $B$ in Eq. (2) cannot be directly compared with the estimate given in ref. [5] because these authors chose $M$ in (2) to be $M_H$.

The harmonic frequency $\nu_o$ is given by the quadratic term:

$$\nu^2 = 2a_2/M.$$

The values of $\nu$ are greater than the quasi-harmonic frequencies calculated from the dynamical matrix as described above. This is because of the inclusion of quartic and other anharmonic terms in $E_{ij}$.

The energy-levels of the anharmonic oscillator, $\omega_n$, were then found using two methods. In the first, we expanded the oscillator wavefunction in eigenfunctions, $\psi_j$, of the harmonic oscillator whose frequency is $\nu$,

$$\Psi_n = \sum_{j=0}^{N} c_{n,j} \psi_j.$$

The coefficients $c_{n,j}$ are found from the secular matrix in the usual way.

This approach is not based on perturbation theory as the number of terms in this expansion can be increased until the energy level converges. In practice for $m$ up to 8, $N$ must be greater than 10 and we used 50 to be certain that accurate estimates of the energy levels had been found. A problem with this method is that the polynomial may have other minima far away from the region of $x$ used to evaluate $E$. These minima are of course quite unphysical but for large enough $N$, the oscillator wavefunction will leak into these unphysical regions and the calculated frequencies will then be incorrect. It is easy to ascertain whether this had occurred by plotting out the wave function. The second approach directly integrates the Schrödinger equation and the eigenvalues are found by the shooting method with the boundary conditions that the oscillator wave function vanishes at the end points of the ranges of $x$ used to calculate $E$. For all the results given here, these two methods gave frequencies within 1 $\mathrm{cm}^{-1}$ of each other. These procedures gave the three lowest eigenvalues of the anharmonic oscillator and hence the fundamental and overtone transition frequencies could easily be found.

There are several ways in which anharmonicity can be quantified. Besides the parameter $B$ defined in Eq. (2), there is the anharmonicity parameter $B_o/M$ which is related to the the difference between the overtone and fundamental frequencies by :

$$B_o/M = 2(\omega_1 - \omega_0) - (\omega_2 - \omega_0). \tag{9}$$

Here $\omega_n$ are the energy levels of the oscillator. $B_o$ vanishes when the potential is harmonic. If the potential was limited to cubic and quartic terms in $x$, then to lowest order perturbation theory, $B$ in Eq. (2) and $B_o$ are then given by:

$$B = B_0 = (15a_3^2 - 12a_2a_4)/8a_2^2. \tag{10}$$

However, $B$ and $B_o$ are not equal in higher order. Accordingly, it is of interest to determine $B$ directly from Eq. (2) and investigate its dependence on mass. The difference between $B$ and $B_o$ is a measure of the importance of terms beyond those considered in low order perturbation theory. Anharmonicity also causes changes in the fundamental frequency with bond length. From a theoretical view-point, this is a most important measure as it limits the accuracy with which the fundamental frequency can be calculated. We shall see below that the major error in the calculations arises from estimates of the equilibrium bond length, and small errors in this quantity lead to much greater differences in the frequencies than the effect of $\chi$ on $M$.

## IV. ANHARMONICITY OF HCN

The *ab initio* method gives equilibrium C-H and C-N bond lengths in the HCN molecule of 1.07 and 1.15 Å, which are to be compared with experimental values of 1.06 and 1.15 Å [7]. The quasi-harmonic frequencies calculated from the dynamical matrix are shown together with the experimental results in Table II. The calculated frequencies are in good agreement with the observed ones even though anharmonicity has been taken into account in a crude way. It is interesting that this molecule has a C-H bend mode close to the $E^-$ mode in the C-H defect in GaAs.

The values of the energy second derivatives are given in Table III. We note that $E_{C,C}$ is particularly large reflecting the strength of the C-N bond. We now suppose the coupling between the N atom and the other two atoms can be neglected so that the dynamical matrix reduces to a 2×2 one. Then inserting the values of $E_{ij}$ from Table III into Eq. (5) and iterating, we find $\chi$ to be 0.77 for H and 0.59 for D. These values are less than unity and as stated above this arises because $E_{C,C}$ (Table III) is particularly large for HCN. These values of $\chi$ when inserted into Eq. (4) yield H and D frequencies of 3305 and 2512 $\mathrm{cm}^{-1}$ respectively. The closeness of the H-mode with the one calculated from the full dynamical matrix shows that the neglect of the movement of N is valid. However, the large discrepancy for the C-D mode reveals that in this case the effect of the vibration of C-N cannot be neglected. The

C-N mode at 1944.5 cm$^{-1}$ interacts strongly with the C-H mode when H is changed to D. The effect of the interaction is similar to that found between the two $E$-modes in the CH defect in GaAs discussed above.

The anharmonic potential for H is calculated by displacing the H atom from a rigid C-N unit, although almost identical results arise if the N atom is relaxed during the stretching of the C-H bond. For each H displacement, the self-consistent energy $E$ was recalculated and its variation with $x$ is shown in Fig. 2. It illustrates the classical character of a negative third order derivative. The potential was evaluated for H displacements from the equilibrium value from -1.0 au to 1.0 au. These values were used to fit $E$ to a polynomial as described above. For $m = 8$, the error in the fitted potential is $7.1\times10^{-5}$au(16 cm$^{-1}$). Table IV gives the resulting coefficients $a_i$ in Eq. (7). The term $a_2$ leads directly to the harmonic frequency, $\nu$, which is 3552.5 cm$^{-1}$ for $\chi = 0.77$. This is much greater than the quasi-harmonic one in Table II which is to be understood as the latter include some anharmonic contributions arising from quartic terms in the potential.

The Schrödinger equation for the oscillator is now solved as described above using this potential and with mass, $M$, given in Eq. 8, with $\chi = 0.77$. Fig. 2 shows the lowest three energy levels and wavefunctions of the oscillator. We note that all three wavefunctions have become negligible at the boundaries of the region used to calculate $E$. If this had not happened, then the polynomial fit to $E$ would have been unreliable in a region where the wavefunction was not negligible. We also note that the wavefunctions have larger peaks for positive $x$ than for negative $x$. This reflects the lower potential experienced when the C-H bond is stretched over its values when it is compressed. This is important when the intensity of the overtone is considered.

The fundamental and overtone frequencies are given in Table V and are about 4% lower than the observed values. The anharmonicity parameter, $B_o/M$, is 106.3 cm$^{-1}$ and is very close to the observed one at 102.3 cm$^{-1}$. Choosing $\chi$ to be unity has little effect on $B_o/M$ (104.0 cm$^{-1}$), although the fundamental frequency is then reduced by 34 cm$^{-1}$. The quasi-harmonic frequencies in Table II lie between the harmonic and anharmonic ones. The principal error in the location of the fundamental frequency comes from its sensitivity to the equilibrium length of the C-H bond. We suppose that the errors in the calculation lead to an additional term in the potential energy that is linear in $x$ and has the effect of decreasing slightly the equilibrium length of the C-H bond from its calculated length of 1.07 Å towards the experimental value of 1.06 Å. Because the potential is so anharmonic, the frequency rapidly increases with decreasing bond length. Fig. 3 shows the variation of the fundamental and overtone frequencies versus the change in bond length. The change in bond length needed to bring both results into agreement with the experimental ones is very small: about -0.011 Å. This shift would also bring the calculated and observed bond lengths into almost complete agreement. $B_o/M$, however, is then 105 cm$^{-1}$ and almost unchanged from its previous value. Thus the anharmonicity parameter depends weakly on the C-H bond length. This implies that *ab initio* theory is able to calculate this quite accurately although the absolute frequencies are much less accurate. The simple theory given here excludes a discussion of the overtone and the parameter $B$ in the deuterated case because of the strong interaction between the C-D and C-N modes.

It is of interest to investigate whether low order perturbation theory can account for anharmonicity in HCN. This can only be done if a quartic potential describes the anharmonic oscillator. However, if the coefficients $a_i, i > 4$ in Eq. (7) are set to zero, then the fundamental and overtone frequencies become 3229.7 and 6448.2 cm$^{-1}$ ($\chi = 0.77$) and the anharmonicity $B_o/M$ is then only 11.2 cm$^{-1}$. Thus this potential is inadequate to account for the large anharmonic effects. An alternative method is to try to fit the potential to a quartic polynomial, i.e. $m$ in Eq. (7) is 4. Of course the error in the fit is now much worse, $\approx 7.8\times10^{-3}$ au, and this potential gave fundamental and overtone frequencies at 1947.2 and 4006.6 cm$^{-1}$. These results show that low order perturbation theory cannot be used to describe the overtone in HCN.

To conclude, $\chi$ is less than unity in the case of the H stretch mode in HCN due to the very strong C-N bond. This also causes a strong interaction between the C-D and C-N modes. The absolute values of the fundamental and overtone modes are very sensitive to the calculated C-H length, although the calculated anharmonicity is less sensitive and its value is very close to that observed. Low order perturbation theory does not quantitatively describe the overtone.

## V. THE $C_{AS}$-H STRETCH MODE IN GAAS

All 87 atoms in the cluster $CGa_{22}As_{21}H_{43}$ with C at a central As site and H near a bond centered site were allowed to relax. The C-H and H-Ga lengths were found to be 1.126 and 2.253 Å. The energy double derivatives were then derived by displacing the six inner atoms by $\pm 0.09$ au and calculating the forces on them. Then the full dynamical matrix was constructed using a Musgrave-Pople potential [29] for the remaining entries. Table I shows the calculated quasi-harmonic and observed modes [27]. The C-H stretch frequency is 11% too high but the calculated local modes of C are in good agreement with the observed ones.

The value of $\chi$ deduced from Eq. (1) using either the observed H and D stretch frequencies for $^{12}$C, or the H and D stretch frequencies for $^{13}$C, yield $\chi$ to be about 0.63. We must now decide whether a value of $\chi$ less than unity reflects a very strong C-X bond as in HCN or an effect due to anharmonicity as suggested in ref. [5]. If the calculated stretch frequencies for H and D for either C isotope in Table I are used to determine $\chi$, then a value of about 1.17 is found. Alternatively, if we neglect the coupling between C and the lattice, then $\chi$ can be calculated directly from Eq. (5) and this gives it to be about 1.23. These results make it certain that, in contrast to HCN, $\chi$ is larger than unity for the C-H stretch mode in GaAs. This shows that the anomalous isotope shifts are to be explained through anharmonic effects in agreement with the conclusions of ref. [5].

We investigated the anharmonicity in the C-H stretch mode in a similar way to that described above for HCN. The energy $E$ was evaluated by displacing H in steps 0.05 au from -1.0 to 1.0 au $E$ was then fitted to a power series up to terms of order 8 and the coefficients found are given in table IV. The error in the potential fit is $2.8\times10^{-5}$ au (6 cm$^{-1}$). Fig. 4 shows this potential as well as the wavefunctions and energy levels of the three lowest states. The curves are rather similar to the HCN case discussed above.

Table VI gives the harmonic, fundamental and overtone frequencies evaluated from the potential using $\chi = 1.23$. The fundamental H-stretch frequency lies at 2963.2 cm$^{-1}$ and, in contrast with HCN, is close to that found from the dynamical matrix. The harmonic frequencies are greater, as expected, than the quasi-harmonic ones of Table I. The anharmonicity parameter, $B_o/M$, is 144.0 cm$^{-1}$ for H and is larger than that found in HCN by almost 36%. If $\chi$ is taken to be unity, then the fundamental and overtone frequencies drop by 20 and 41 $\mathrm{cm}^{-1}$ respectively, leaving $B_o$ virtually unchanged.

Such large anharmonicities must imply a great sensitivity of the calculated frequency with the C-H bond length and can account for the overestimate in the C-H stretch frequency. The C-H force constant is the second derivative of the potential and the contribution of the cubic term in Eq. (7) shows that this decreases with increasing $x$ by a factor

$$(1 + 3a_3x/a_2).$$

Inserting the values of the coefficients from Table IV, we find this factor is 0.82 when $x$ is only 0.056 au(0.03 Å). This would lead to a drop in the frequency by about 9%. A more rigorous approach is to solve the Schrödinger equation for the oscillator when an additional term linear in $x$ has been added to the potential. Fig. 5 shows the variation in the fundamental and overtone transition frequencies with the change in the length of the C-H bond in this case. It is seen that the experimental fundamental frequency is reproduced when the C-H length is only 0.035 Å longer than that calculated by the *ab initio* method. However, the anharmonicity parameter is again rather insensitive to the bond length. $B_o/M$ is now found to be 156 $\mathrm{cm}^{-1}$ – about 47% larger than for HCN.

It is of interest to determine the dependence of the anharmonicity parameters $B_o$ and $B$ in Eq. (2) on the oscillator mass $M$. Fig. 6 shows this behavior for the *ab initio* C-H bond length of 1.126 Å as well as the extended length of 1.161 Å necessary to obtain agreement with the observed fundamental. The values of $B$ and $B_o$ rapidly approach their asymptotic values given by low order perturbation theory for $M$ greater than 1 in the first case and about 1.8 in the second. The importance of higher order terms in perturbation theory is much greater for $B_o$ than for $B$ because the wavefunction of the oscillator in the second excited state samples a much greater range of the potential. These results suggest that low order perturbation theory provides a reliable guide for calculating the effects of anharmonicity. This however is quite wrong.

If the coefficients $a_i$ in Eq. (7) are set to zero for $i > 4$, then the fundamental and overtone H frequencies become 2988 and 5897 $\mathrm{cm}^{-1}$ for $\chi$ and C-H to be 1.23 and 1.126 Å. Hence the anharmonicity parameter $B_o/M$ drops to 79 $\mathrm{cm}^{-1}$. $B$ still approaches its asymptotic value of Eq. (10) given by low order perturbation theory for large $M$ but the rapid approach to the asymptotic value is only valid for certain ranges of the coefficients $a_i, i > 4$ and outside these ranges, masses very much bigger than unity are needed for $B$ to be given by its asymptotic value. This means that low order perturbation theory is inapplicable. If the potential was fitted with a quartic polynomial, then of course the error in the fit is much larger and the frequencies of the fundamental and overtone then become 2897 and 4269 $\mathrm{cm}^{-1}$. This leads to an anharmonicity parameter $B_o/M$ equal to 338 $\mathrm{cm}^{-1}$. We therefore conclude that perturbation theory cannot be used to describe the parameters $B$ and $B_o$.

In summary, the calculated effective mass parameter $\chi$ is greater than unity for the case of C-H in GaAs but anharmonic effects are particularly large. This makes the calculated transition frequencies depend critically on the C-H length although the anharmonicity parameter and isotope shifts are not as sensitive. An increase in length of the C-H bond by as little as 0.035 Å brings the calculated fundamental frequency into agreement with the observed frequency. The anharmonicity parameter $B$ is about 160 amu $\mathrm{cm}^{-1}$ and close to the estimate of 176 amu $\mathrm{cm}^{-1}$ given in ref. [5]. The anharmonicity is sensitive to high order derivatives in the potential energy and it effects cannot be described by low order perturbation theory.

## VI. THE INTENSITY OF THE OVERTONE

Given the anharmonicity is so large, it is puzzling that the overtone has not been reported. One possibility is that the electrical anharmonicity has an important effect in reducing its intensity to below the limit of detection. We show in Fig. 7 the dipole moment, $p(x)$, of the cluster. It is clear that this is a convex function whose curvature leads to important effects in the intensity of the overtone. The ratio of the intensities in the overtone and fundamental can be found from the relation:

$$I = \left( \frac{\int \Psi_2(x)p(x)\Psi_0(x)dx}{\int \Psi_1(x)p(x)\Psi_0(x)dx} \right)^2 . \tag{11}$$

The wavefunctions associated with the oscillator are shown in Fig. 4. The numerator in Eq. (11) vanishes if $p(x)$ is either a constant or, if mechanical anharmonicity is absent, is linear in $x$. This follows because the wavefunctions are orthogonal and have the same parity. When mechanical anharmonicity is included parity is no longer a quantum number and the maximum in $|\Psi_n(x)|$ is larger for positive $x$ than for negative $x$. This is a consequence of the lower potential energy in the region $x > 0$. Now, the product of wavefunctions in the numerator in Eq. (11) is shown in Fig. 7 and is positive for $x$ between the nodes in $\Psi_2$ and negative otherwise. As the dipole $p(x)$ increases rapidly for positive values of $x$, then regions beyond the upper node become more important and lead to a decrease in the integral. Hence we expect electrical anharmonicity to decrease the intensity of the overtone.

If we carry out the integral with the *ab initio* values of $p(x)$ we find the intensity ratio is 0.0033 for the C-H length to be 1.126 Å. If we neglect electrical anharmonicity and assume that $p(x)$ is linear in $x$, we get an intensity ratio of 0.016. Thus electrical anharmonicity leads to a reduction in the intensity of 79%. If we use the slightly longer C-H length which brings the calculated and observed fundamental transition frequencies into agreement, then these ratios become 0.0028 and 0.010 respectively. This gives a 72% reduction. It is of interest to see the effect of gradually increasing the magnitude of electrical anharmonicity. This can be done by fitting the dipole moment $p(x)$ to a polynomial in $x$ and multiplying the non-linear terms by factor of $\lambda$. Electrical anharmonicity is absent for $\lambda$ is 0.0 and fully present when $\lambda$ is unity. We show in Fig. 8 the effect of the varying electrical anharmonicity on $I(\lambda)/I(0)$. It is clear that there is a value for electrical anharmonicity for which the overtone cannot be detected at all!

## VII. CONCLUSIONS

Our conclusions are :

1. $\chi$ defined by Eq. (1) need not always be greater than unity if the C atom is strongly bonded to another species. This is the case for the C-H stretch mode in HCN and this could also occur for defects in solids, e.g. H-O-X defects etc. Indeed the value of $\chi$ could be used as a measure of the O-X strength.

2. Local density functional cluster theory gives a good account of the anharmonic vibrations of molecules and defects in solids. The effects of anharmonicity are most important for the accurate location of bond frequencies: a slight error in bond length having a disproportionate error in frequency. As a rule of thumb, it appears that a 3% change in bond length causes a 10% change to frequency. It is this sensitivity that led us initially to a extremely good estimate of the C-H frequency in GaAs and an over-estimate in the present calculation.

3. The anharmonicity parameter $B_o$ deduced from the overtone, is 50% larger for C-H encapsulated in a solid than for HCN. This is probably due to the confining effect of the Ga atom along the C-H axis. This is supported by the fact that the anharmonicity parameter, $B_o$, for the C-H stretch mode in GaAs, is much greater than that for the C-H bond on the $\langle 111 \rangle$ diamond surface (113 $cm^{-1}$ [8]). This suggests that evidence for bond centered configurations might be found from knowledge of the anharmonicity parameters, $B$ and $B_o$.

4. Low order perturbation theory cannot be used to give a quantitative account of anharmonicity.

5. The intensity of the overtone is reduced by a factor of 0.79 by electrical anharmonicity. The dipole moment itself is a convex function which is almost independent of the C-H length for compressed bonds but increases rapidly with extended ones. The overtone intensity is a very sensitive function of electrical anharmonicity and can in principle be reduced to zero. Observations by Darwich et al [6] of overtones due to P-H bonds in InP where Zn and Cd acceptors are passivated with H in a bond-centered position show that the P-H overtone intensity is close to half that expected from a simple Morse potential. This is almost certainly because electrical anharmonicity has been neglected.

The overtone of the C-H stretch mode in GaAs has not been reported to-date. This may reflect the reduction in the intensity because of electrical anharmonicity, as this effect can be very large. Alternatively, it may be a consequence of a very short lifetime of the mode. It is noteworthy that the energy of the overtone, 0.6 eV, is larger than the adiabatic barrier for re-orientation of H around the four <111> axes. Thus the lifetime of the anharmonic oscillator might be extremely short due to coupling with this or with other modes.

## ACKNOWLEDGMENTS

We thank Ron Newman for many stimulating discussions during the course of this work. S Ö thanks the Swedish National Scientific Research Council, for financial support.

## TABLES

TABLE I. Calculated and Observed LVM's, $cm^{-1}$, due to C-H in GaAs and AlAs

| | Obs. GaAs [27,25] | Theory GaAs | Obs. AlAs [24,27] | Theory AlAs |
|---|---|---|---|---|
| $^{12}$C-H | 2635 | 2950 | 2558 | 2885 |
| $^{13}$C-H | 2628 | 2942 | 2549 | 2877 |
| $^{12}$C-D | 1969 | 2154 | 1902 | 2111 |
| $^{13}$C-D | 1958 | 2144 | 1894 | 2100 |
| $A_1$ modes | | | | |
| $^{12}$C-H | 453 | 456 | 487 | 466 |
| $^{13}$C-H | 438 | 440 | 477 | 453 |
| $^{12}$C-D | 440 | 442 | 480 | 454 |
| $^{13}$C-D | 427 | 428 | 471 | 442 |
| $E^-$ H-like modes | | | | |
| $^{12}$C-H | 739 | 888 | 671 | 740 |
| $^{13}$C-H | 730 | 883 | 653 | 725 |
| $^{12}$C-D | 637 | 707 | 657 | 684 |
| $^{13}$C-D | 617 | 693 | 635 | 662 |
| $E^+$ C-like modes | | | | |
| $^{12}$C-H | 563 | 553 | ND | 559 |
| $^{13}$C-H | 548 | 536 | ND | 551 |
| $^{12}$C-D | 466 | 495 | ND | 437 |
| $^{13}$C-D | 464 | 487 | ND | 436 |

TABLE II. Calculated and Observed Frequencies, $cm^{-1}$, of Modes of H-C-N

| H-$^{12}$C | | D-$^{12}$C | |
|---|---|---|---|
| Calculated | Observed | Calculated | Observed |
| 3318.9 | 3312 | 2611.5 | 2629 |
| 2125.0 | 2089 | 1944.5 | 1906 |
| 764.3 | 712 | 609.1 | 569 |

TABLE III. Calculated Double Derivatives for H-C-X in au

| System | $E_{C,C}$ | $E_{C,H}$ | $E_{H,H}$ |
|---|---|---|---|
| HCN | 1.565 | -0.374 | 0.376 |
| HC-(GaAs) | 0.342 | -0.277 | 0.311 |

TABLE IV. Calculated Coefficients for $E$ in au

| System | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $a_6$ | $a_7$ | $a_8$ |
|---|---|---|---|---|---|---|---|
| HCN | 0.1846 | -0.1932 | 0.1473 | -0.0780 | 0.0234 | -0.0265 | 0.0210 |
| HC-(GaAs) | 0.1703 | -0.1771 | 0.1025 | -0.0503 | 0.0378 | -0.0225 | 0.0047 |

TABLE V. Calculated and Observed Anharmonic C-H Frequencies, $cm^{-1}$, of HCN

| Mode | $\chi = 0.77$ | $\chi = 1.0$ | Observed |
|---|---|---|---|
| Fundamental | 3189 | 3155 | 3312 |
| Overtone | 6273 | 6206 | 6521.7 |
| Anharmonicity, $B_o/M$ | 106.3 | 104.0 | 102.3 |

TABLE VI. Calculated and Observed Anharmonic C-H Frequencies, $cm^{-1}$, of C in GaAs

| Mode | Obs. [5,10,11] | Harmonic | $\omega_1 - \omega_0$ | $\omega_2 - \omega_0$ | Mass (amu) | $B$ | $B_o$ |
|---|---|---|---|---|---|---|---|
| C-H = 1.126 Å, | | | | | | | |
| $^{12}$C-H | 2635 | 3108.1 | 2963.2 | 5782.3 | 0.937 | 135.7 | 134.9 |
| $^{13}$C-H | 2628 | 3100.5 | 2956.3 | 5769.2 | 0.941 | 135.7 | 134.9 |
| $^{12}$C-D | 1969 | 2266.4 | 2189.3 | 4301.2 | 1.761 | 135.8 | 136.3 |
| $^{13}$C-D | 1958 | 2256.0 | 2179.6 | 4282.5 | 1.778 | 135.8 | 136.3 |
| C-H = 1.161 Å | | | | | | | |
| $^{12}$C-H | 2635 | 3012.8 | 2635.2 | 5114.3 | 0.937 | 159.1 | 146.2 |
| $^{13}$C-H | 2628 | 3005.5 | 2629.1 | 5102.7 | 0.941 | 159.1 | 146.5 |
| $^{12}$C-D | 1969 | 2196.9 | 1954.5 | 3819.0 | 1.761 | 160.3 | 158.4 |
| $^{13}$C-D | 1958 | 2186.8 | 1945.9 | 3802.7 | 1.778 | 160.3 | 158.4 |

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## Figure Captions

Figure 1: The $C_{As}$-H defect in GaAs.

Figure 2: (a) Potential energy (au) versus displacement from equilibrium, $x$, (au) for C-H stretch in HCN. The oscillator wavefunctions for the ground (b), first (c) and second (d) excited states are also shown. The horizontal lines show the energies of these states.

Figure 3: The variation of the fundamental (a) and overtone (b) frequencies in $cm^{-1}$ with the change in the equilibrium C-H length (Å) in HCN. Curve (c) shows the the fundamental frequency $\times 2$ and its difference from (b) demonstrates that the anharmonicity varies slowly with the C-H length. The horizontal lines show the experimental frequencies (3312 and 6521.7 $cm^{-1}$) [7]).

Figure 4: (a) Potential energy (au) versus displacement from equilibrium, $x$, (au) for C-H stretch in GaAs. The oscillator wavefunctions for the ground (b), first (c) and second (d) excited states are also shown. The horizontal lines show the energies of these states.

Figure 5: The variation of the fundamental (a) and overtone (b) frequencies in $cm^{-1}$ with the change in the equilibrium C-H length (Å) for C-H in GaAs. Curve (c) shows the the fundamental frequency $\times 2$ and its difference from (b) demonstrates that the anharmonicity varies slowly with the C-H length. The horizontal line shows the experimental frequency (2635.2 $cm^{-1}$ [5]).

Figure 6: The variation of the anharmonicity parameters (amu $cm^{-1}$) with $1/\sqrt{M}$. Curves (a) and (b) are $B$ and $B_o$ for the C-H length = 1.126 Å and (c) and (d) are $B$ and $B_o$ for the extended length of 1.161 Å. The crosses denote values of the mass for $^{12}$C-H, $^{13}$C-H, $^{12}$C-D and $^{13}$C-D.

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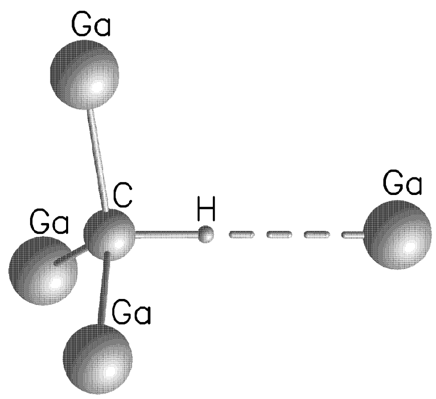
Figure 8: The intensity of the overtone versus the degree of electrical anharmonicity $\lambda$. The C-H length is 1.126 Å in curve (a) and 1.161 Å in curve (b).

FIGURES

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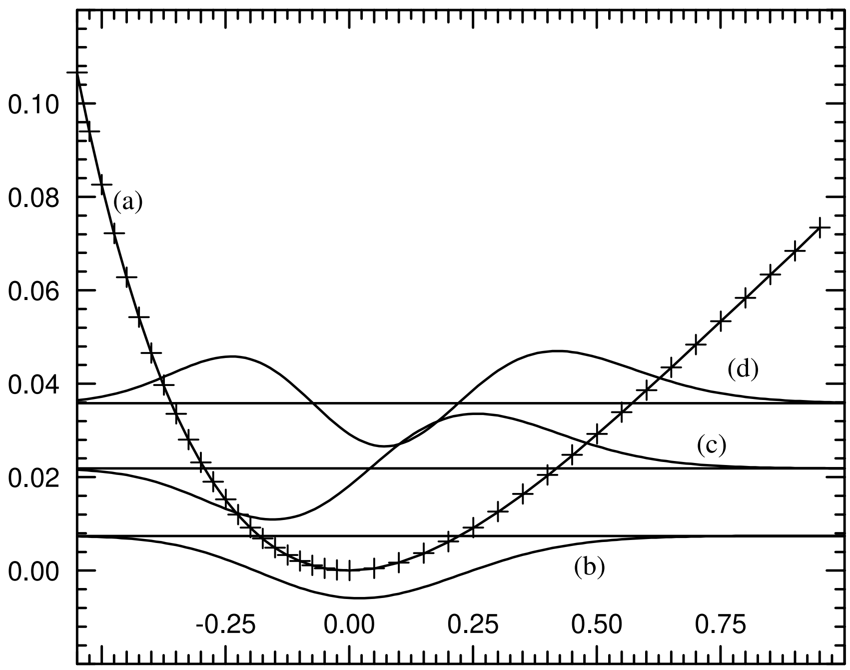


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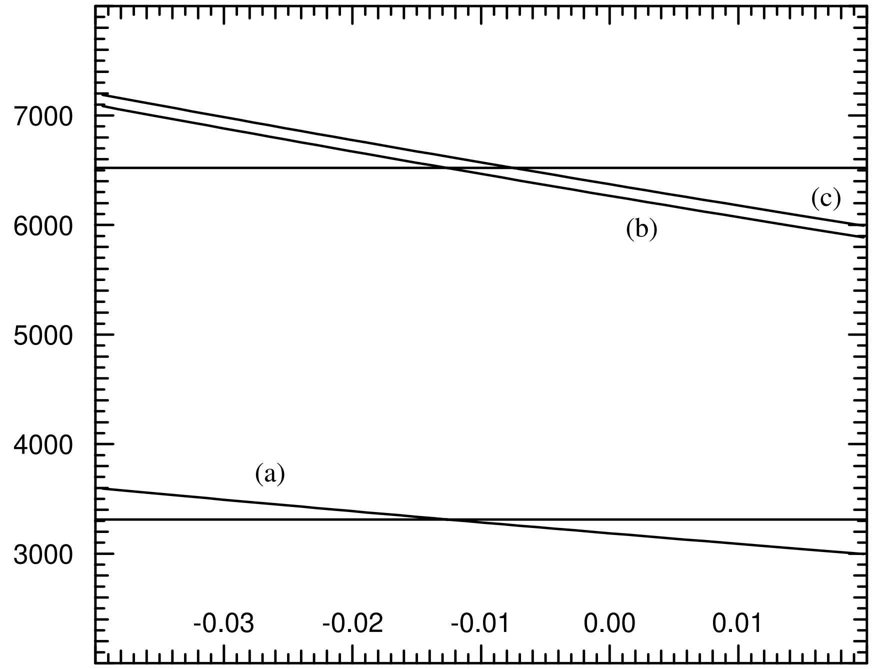


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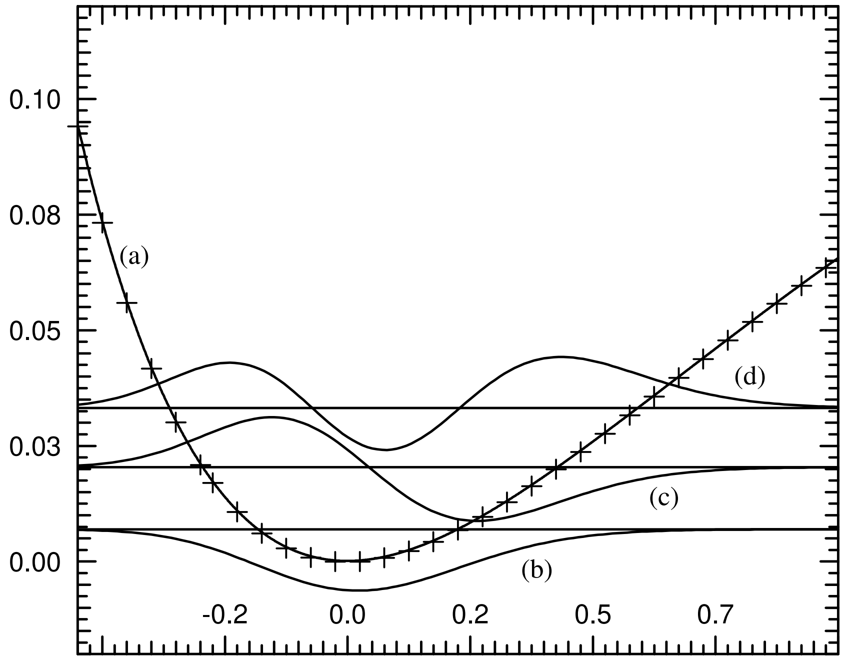


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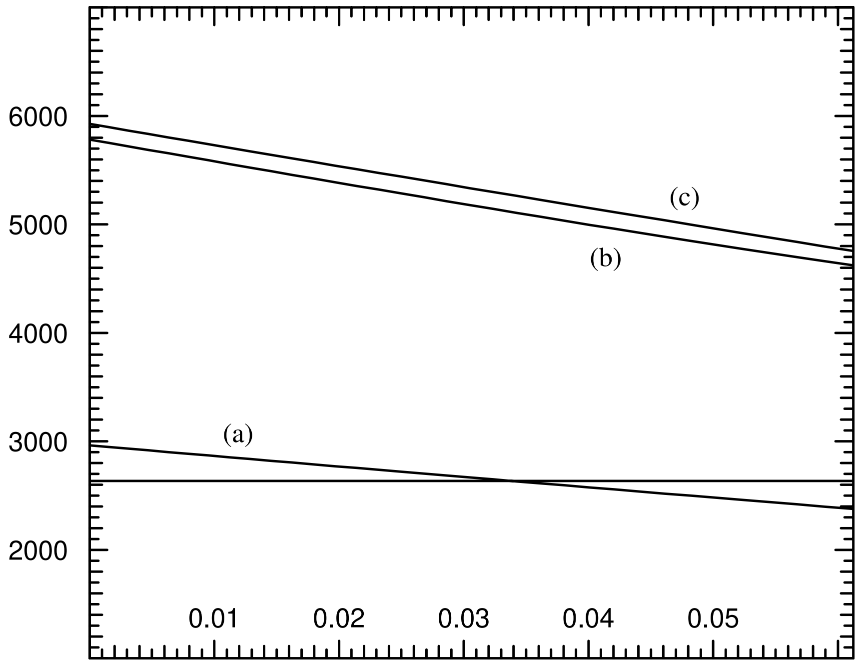


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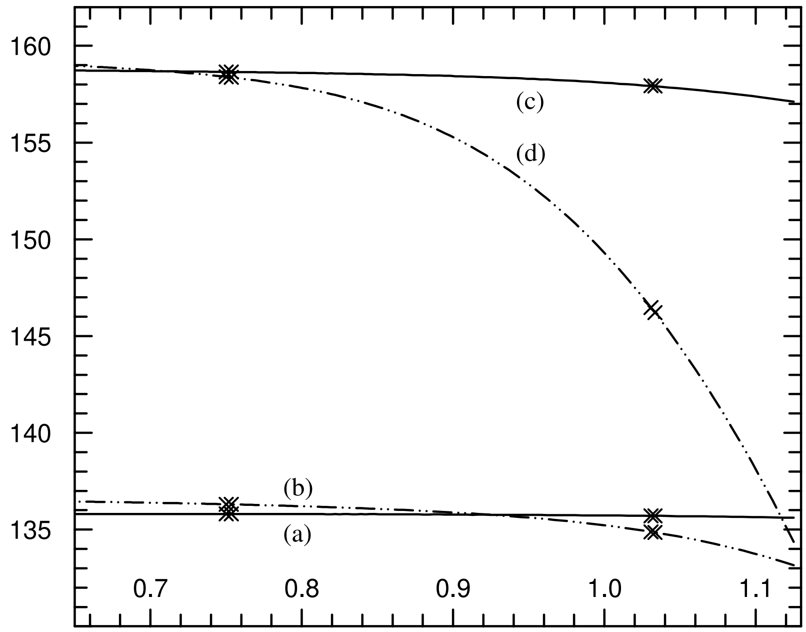


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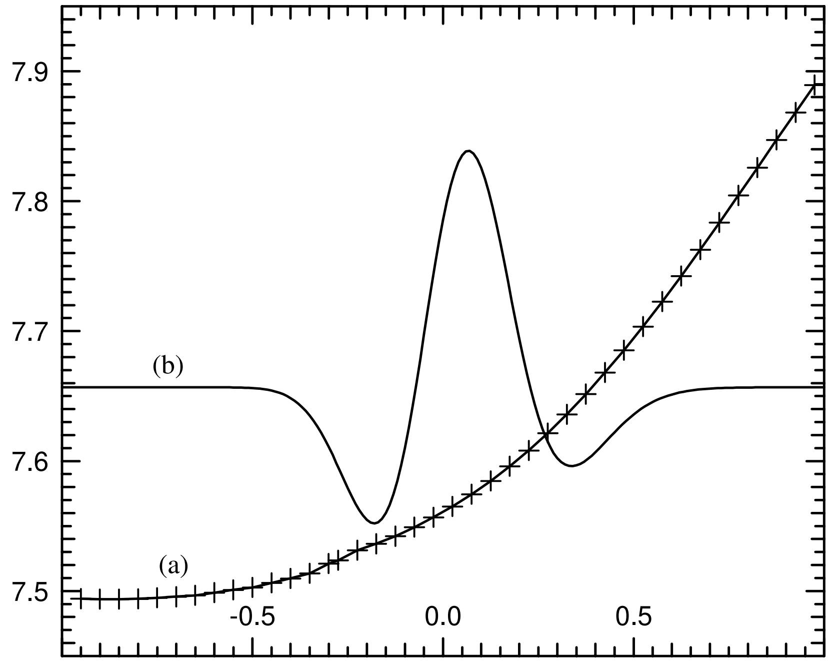


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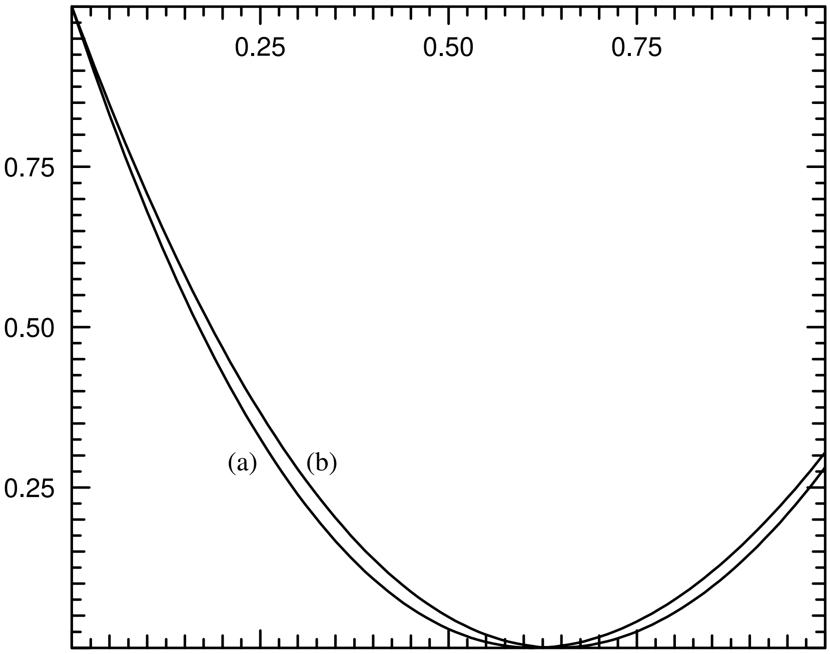


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