Structure and vibrational properties of the PTCDA/Ag(1 1 1) interface: bilayer versus monolayer

N L Zaitsev¹,², P Jakob³ and R Tonner⁴

¹ Laboratory of Theoretical Physics, Institute of Molecule and Crystal Physics—Subdivision of the Ufa Federal Research Center of the Russian Academy of Sciences, 450075, Ufa, Russia
² Laboratory of Nanostructured Surfaces and Coating, Tomsk State University, 634050, Tomsk, Russia
³ Department of Physics, Philipps-Universität Marburg, 35032, Marburg, Germany
⁴ Department of Chemistry, Philipps-Universität Marburg, 35032, Marburg, Germany

E-mail: nza@yandex.ru

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Abstract
The structural and vibrational properties of metal–organic interfaces have been examined by means of infrared (IR) absorption spectroscopy and density functional theory (DFT) with an approach accounting for long-range dispersive interactions. We focus on a comparative study of the PTCDA monolayer and bilayer on Ag(1 1 1). The equilibrium geometry at the molecule-metal interface and the IR spectrum of the chemisorbed monolayer of PTCDA on Ag(1 1 1) are well described by the computations. In the bilayer structure, the presence of a physisorbed adlayer on top of PTCDA/Ag(1 1 1) presents a challenge for DFT. As previously described for other systems, the polarization of the substrate is not captured correctly and results in too low energies of frontier molecular orbitals. This results in an apparent contribution from the vibrations of second-layer PTCDA to the IR spectrum due to interfacial dynamical charge transfer processes. After removing these peaks with artificially strong intensity, calculated and experimental data show good agreement and the IR spectrum can be described as the sum of the spectra of the PTCDA/Ag(1 1 1) contact layer and a physisorbed PTCDA monolayer on top.

Keywords: metal–organic interface, vibrational spectroscopy, vdW-DFT calculation, infrared spectrum

(Some figures may appear in colour only in the online journal)
range van der Waals (vdW) forces within DFT calculations [24, 25], which is crucial for calculating accurate adsorption geometries. Thus, PTCDA/Ag(1 1 1) is an excellent prototype system for exploring the influence of the second layer on the properties of the first one.

Despite the vast opportunities of vibrational spectroscopy to characterize organic layers on metal surfaces, very few studies on the vibrational properties of PTCDA/Ag(1 1 1) exist [26–28]. In a recent study, the high intrinsic spectral resolution of infrared (IR) absorption spectroscopy has been used to detect the vibrational line shifts of only a few wavenumbers associated with different numbers of layers of deposited molecular species, e.g. of bilayer, trilayer or multilayer [28, 29]. The respective characteristic, layer-dependent vibrational modes can be extracted from the experiment and compared to DFT calculations. On the one hand the experimental spectra are interpreted within a well established ab initio framework, and on the other hand the accuracy of DFT calculations are put to the test by precise experimental methods. Note, that the reproduction of the vibrational properties of metal–organic interfaces is a challenge for the current approximate exchange-correlation functionals used for DFT computations insofar as a simultaneous and accurate description of the adsorption geometry, energy level alignment and dipole layer formation are needed.

In the present study, we have examined PTCDA/Ag(1 1 1) molecular layers by means of IR absorption spectroscopy and vdW-DFT calculations. The focus was on a comparative study of the vibrational properties of the monolayer and bilayer of PTCDA molecules on Ag(1 1 1). Here we confirm that already a monolayer of organic molecules creates a metal–organic interface, and the interface properties are altered only slightly by increasing the thickness of the organic adlayer.

2. Methods

Calculations were done using DFT as implemented in the SIESTA code [30, 31]. Localized pseudoatomic orbitals were used for the wave function representation together with norm-conserving pseudopotentials [32]. Long-range dispersion forces were described by using the optB88-vdW functional approach [33, 34].

The scheme of periodically repeated slabs was used to describe the Ag(1 1 1) surface. Interactions between the periodic images of the system in the direction perpendicular to the surface (z-direction) was suppressed by a vacuum layer of about 11 Å. The slab dipole correction was used to avoid the artificial macroscopic electrostatic field which arises due to the periodic boundary conditions [35, 36]. A uniform mesh for the numerical integration and solution of the Poisson equation was specified by the energy cutoff of 400 Ry. The molecular adsorbate was applied to one side of the substrate only. The surface Brillouin zone sampling was done by 8 k-points with use of the Monkhorst–Pack scheme. Atomic positions were optimized until the forces were smaller than 0.01 eV Å⁻¹. During the relaxation the substrate was represented by four layers of atoms with the bottom two layers fixed to bulk position.

The double-ζ polarized (DZP) basis set with an energy shift of 10 meV and generated by a soft confinement scheme was used for all atoms in the molecule. Two types of basis functions for silver atoms were used. External atoms of the slab in the upper- and lowermost silver layers have a cutoff radius \( r_c = 9.73 \) a.u. of the 5s orbitals (energy shift is 10 meV); for the other atoms and the remaining internal Ag atoms \( r_c = 7.03 \) a.u. has been used (energy shift is 180 meV). The same parameters were used and justified in our recent works [37, 38]. The silver lattice constant was set to its equilibrium value of \( a = 4.17 \) Å⁻¹, as was found from the calculation with the short \( r_c \) basis functions.

Vibrational properties were calculated via diagonalization of the dynamical matrix within the harmonic approximation. Finite displacements of ±0.02 Å⁻¹ of individual atoms in each spatial direction were used to build the dynamical or force-constant matrix. The sum rule which follows from Newton’s third law was imposed onto the force constant matrix to ensure that the force acting on the displaced atom was exactly the sum of the forces acting on the other atoms in the unit cell [39]. A detailed description of the procedure we were following here to get the vibrational frequencies can be found in [40].

The vibrational analysis was carried out in the frozen surface approximation. Only atoms of the PTCDA molecules were displaced for construction of the Hessian [41], and Ag atoms were kept fixed at their equilibrium positions. This is motivated by the large difference in atomic mass between the light atoms of the adsorbate and the heavy silver atoms. IR intensities were calculated as the square of dipole moment light atoms of the adsorbate and the heavy silver atoms. IR intensities were calculated as the square of dipole moment derivatives with respect to the normal-mode coordinate [42]. Because of the periodicity of the system in xy-directions and the metallic nature of the Ag substrate, only the \( z \)-component of the dipole moment was considered in the calculation. To visualize the IR spectrum, every vibrational mode was broadened by a Lorentzian line shape (\( \frac{a}{\pi (\sigma^2 + \sigma^2)} \)) with \( \sigma = 2 \) cm⁻¹ and the corresponding amplitude equals to the calculated IR intensity.

3. Results

It is well established, [8, 11, 43] that PTCDA molecules form an ordered monolayer on Ag(1 1 1). A herringbone arrangement with two molecules per unit cell occupying nonequivalent adsorption sites has been found (figure 1). More recently, the adsorption geometry of PTCDA/Ag(1 1 1) was measured with high accuracy using NIXSW [9, 10] and calculated structures (vdW-DFT) were found to be in good agreement with the experimental ones [24, 25].

3.1. Adsorption geometry

The optB88-vdW exchange-correlation functional used here has provided equilibrium adsorption geometries of the PTCDA/Ag(1 1 1) monolayer in reasonable agreement with the experimental measurements [10, 45]. The two inequivalent molecules in the unit cell (labeled A and B, see figure 2(a))
are bent along the long axis; thereby, the anhydride oxygen atoms reside higher from the substrate than the acylic ones, with adsorption distances of \( \sim 2.7 \, \text{Å}^{-1} \) which is quite close to the experimental value \([10]\) of \( (2.66 \pm 0.03) \, \text{Å}^{-1} \) (see figures 2(a) and (b)) (for details see supporting information (stacks.iop.org/IPhysCM/30/354001/mmedia)). Like in many vdW-DFT calculations, \([24, 25, 45]\) the carbon core adsorption distance of \( \sim 3.05 \, \text{Å}^{-1} \) is noticeably overestimated in comparison to the experiment \((2.86 \pm 0.01) \, \text{Å}^{-1}\), \([10]\) whereas the anhydride oxygen atom’s adsorption height of \( \sim 2.85 \, \text{Å}^{-1} \) underestimates the experimental value of \( (2.98 \pm 0.08) \, \text{Å}^{-1} \). Our previous calculations of the similar system of NTCDA/Ag(111) performed with the same method and parametrization \([37]\) gave a similar picture of the adsorption geometry.

Based on experimental data, it was proposed \([11, 28]\) that PTCDA molecules in the top layer of the bilayer structure have the same lateral order as in the contact layer but the relative positions of the atoms in the top layer could not be identified. We thus checked different layer stackings in the bilayer structure (denoted as P/P/Ag(111)). The first structure (figure 1, top panel) represents the stacking of the layers in the \( \alpha \)-modification of the molecular crystal of PTCDA \([44]\) (denoted as \( \alpha \)-P/P/Ag(111) or \( \alpha \)-stacking). The second structure results from shifting the top layer laterally (denoted as \( \gamma \)-stacking to avoid confusion with the \( \beta \)-modification of the PTCDA molecular crystal \([44]\)). We found the energy difference between the structural arrangements to be negligible (<0.01 eV/cell).

The adsorption height of the contact layer is noticeably altered due to interaction with the second adlayer. This is apparent in figure 2, where the deviation of vertical adsorption distances from a plane positioned 3 Å \( \sim \) above the extrapolated bulk position of the topmost silver layer of P/P/Ag(111) is depicted. Regarding \( \gamma \)-stacked layers, the carbon atoms of the perylene core get closer to the substrate by about 0.1 Å \( \sim \) (figures 2(b) and (c)), whereas some acylic oxygen atoms move away by \( \sim 0.2 \, \text{Å}^{-1} \). Even stronger distortions of the first layer are found for \( \alpha \)-P/P/Ag(111).

The second layer in both structures is distorted as well. As is clearly visible in figures 2(e) and (f) the atomic positions in this layer deviate considerably from the planar geometry for both stacking types. Thereby the averaged interlayer distance in the \( \alpha \)-stacked bilayer is larger by \( \sim 0.1 \, \text{Å}^{-1} \) as compared to \( \gamma \)-stacked layers.

### 3.2. Vibrational properties and IR spectra

Based on the obtained equilibrium structures, we performed calculations of force-constant matrices for further analysis of the vibrational properties and IR spectra.

#### 3.2.1. PTCDA/Ag(111) monolayer

In the range of 600–900 cm\(^{-1}\) there are three groups of prominent peaks in the experimental IR spectrum (shaded area in figure 3) and they are well reproduced by the calculated vibrational modes of PTCDA/Ag(111) (black curve), although they display significantly shifted frequencies (about 60 cm\(^{-1}\)) with respect to the experimental values. For planar molecular adsorbates with their \( \pi \)-conjugated backbone oriented parallel to the surface the spectral range above and below 900 cm\(^{-1}\) is dominated by in-plane and out-of-plane modes, respectively.

Interestingly, the vibrational bands at 600–900 cm\(^{-1}\) consist of two splitted peaks. These spectrally close bands are well reproduced by the calculation and they can be associated with the two inequivalent molecules A and B interacting differently with the Ag(111) substrate. This becomes more obvious when comparing the calculated IR spectra of a free-floating PTCDA monolayer (blue curve) to PTCDA adsorbed on Ag(111).
Specifically, the contact to Ag(111) manifests itself in a frequency downshift by about 40 cm\textsuperscript{-1} and an increased peak splitting for each group. Since vibrational modes in this region are IR-active because of their out-of-plane movement of adsorbate atoms, the increased peak separation most likely is a consequence of the unequal adsorbate-substrate interaction.

The in-plane vibrational modes in the region between 1000 and 1700 cm\textsuperscript{-1} are quite prominent in the PTCDA/Ag(111) experimental and calculated spectra (black line, figure 3), while they are completely absent in the IR spectrum of the free PTCDA monolayer. Apparently, they appear only in the presence of a metallic substrate; this is because the vibrational dipole moment is enhanced due to interfacial dynamic charge transfer (IDCT) between the metal and the molecular layer [46–49]. For comparison, the blue vertical bars in figure 3 denote the line positions of the various totally symmetric in-plane vibrational modes for the free-floating PTCDA monolayer.

When visualizing the oscillatory motion of atoms within the PTCDA molecule, the individual symmetry of each mode can be derived. In the case of in-plane modes of PTCDA all but a few weak bands at 1091, 1181 and 1389 cm\textsuperscript{-1} belong to the A\textsubscript{1} (totally symmetric) irreducible representation of the C\textsubscript{2v} symmetry group. The mentioned weak features belong to
the $A_2$ irreducible representation; they become dipole active due to a local symmetry reduction $C_{2v} \rightarrow C_2$ as a consequence of neighboring PTCDA and the herringbone arrangement of PTCDA/Ag(111).

As in the case of out-of-plane modes, the overall shape of the experimental spectrum at $\omega > 1000$ cm$^{-1}$ is well reproduced by the calculated spectrum of the PTCDA/Ag(111) contact layer. Note that the broad bands in the experimental spectrum at about 1230 and 1540 cm$^{-1}$ are severely influenced by anharmonic coupling of weak combination/overtone bands with nearby strong fundamental modes ($\rightarrow$Fermi resonance coupling) and associated intensity transfer [47, 50, 51]. Such couplings cannot be captured with our current approach of calculating vibrational mode frequencies and intensities, i.e. reproduction of the sub-structure of these bands is not possible. This extra complexity in the vibrational spectrum is particularly obvious in the 1500–1580 cm$^{-1}$ region where the calculation yields a single intense band at 1530 cm$^{-1}$, corresponding to a C-C bond stretching vibration along the longitudinal axis of the molecule. This shows the limit of the currently employed approximations.

The two closely spaced bands at $\sim$1630 cm$^{-1}$ deserve special mention; they correspond to stretching modes of the C–Oacyl bonds of the molecules A and B (figure 3) and, upon adsorption, they are more strongly shifted to lower frequencies as compared to other modes. This was already previously ascribed to the covalent interaction of acyl oxygen atoms with nearby Ag atoms of the substrate [48].

3.2.2. PTCDA/Ag(111) bilayer. A comparison of experimental spectra associated with the mono- and bilayers of PTCDA on Ag(111) shows that the effect of the second adlayer on the vibrational spectrum primarily concerns the out-of-plane modes at $<1000$ cm$^{-1}$ and is minor at $>1000$ cm$^{-1}$ (figure 4); in-plane modes of second-layer PTCDA apparently exhibit zero or near-zero dynamic dipole moments. This means that interfacial dynamical charge transfer (IDCT), which is the main cause of the pronounced intensity of first-layer PTCDA in-plane modes, is not operative for second-layer PTCDA.

The red curves in figures 3 and 4 (bottom panel) refer to the IR spectrum of the PTCDA/Ag(111) bilayer, calculated with the second layer being pinned to its equilibrium geometry (i.e. the force-constant matrix contains only atomic displacements in the first layer). Despite noticeable differences in adsorbate-substrate vertical separation of PTCDA/Ag(111) in comparison with P/P/Ag(111) (figures 2(b)–(d)) the line positions of the various modes of the PTCDA contact layer are changed insignificantly (see figure 3), i.e. the peaks are shifted by few wave numbers only. This clearly demonstrates that the mere presence of a second PTCDA adlayer has a distinct, but only slight effect on the calculated IR spectrum of the PTCDA contact layer. Furthermore, according to the red line and gray shaded area on figure 4 this also holds for vibrations of first-layer PTCDA when the motion of atoms in both layers are explicitly included into the dynamical matrix.

In the region of out-of-plane vibrational modes three additional peaks (figure 4) emerge in the calculated full spectrum.
of γ-P/P/Ag(1 1 1); in accordance with the measurements, their frequencies are shifted towards the blue. Their line positions are very similar to those of the free-floating PTCDA monolayer, which indicates that second-layer PTCDA is interacting only weakly with the underlying molecular layer as well as the Ag(1 1 1) substrate. This conclusion is corroborated by the narrow line shapes (and accordingly significantly enhanced peak intensities) of the respective bands in figure 4 (top panel).

Surprisingly, a fair number of frequency-shifted new peaks appear in the calculated full spectrum at \( \omega > 1000 \text{ cm}^{-1} \), i.e. in the spectral region of in-plane vibrational modes (gray shaded area in bottom panel of figure 4). Comparison to the red curve in the bottom panel of figure 4 suggests that these additional features stem from vibrations of the topmost adlayer. These shifts are quite small \( \sim 10 \text{ cm}^{-1} \) for the two central peaks at \( \sim 1300 \text{ cm}^{-1} \) and \( 1380 \text{ cm}^{-1} \), while somewhat larger values \( (\sim 30 \text{ cm}^{-1}) \) are found for the prominent band at \( 1555 \text{ cm}^{-1} \) and the weak feature at \( 1270 \text{ cm}^{-1} \) (see figure 4). A particularly pronounced shift is observed for the C–Oacyl stretching mode (located at about \( 1600 \text{ cm}^{-1} \) for first-layer PTCDA) which is located at \( \sim 100 \text{ cm}^{-1} \) higher frequencies for second-layer species.

The vibrational frequencies and their patterns of movement are virtually the same for the top-layer of PTCDA and a free PTCDA monolayer sheet. In striking contradiction to the experimental observations, however, the dynamic dipole moments of these new bands are substantial for the top-layer. Note that their intensity cannot be ascribed to slight deformations of the planar structure or a possible tilt, as a very similar spectral signature is found for a perfectly flat second adlayer (figure 4 blue curve).

As discussed above (and more thoroughly in the literature [47–49]) the only way that in-plane vibrational modes of parallel adsorbed PTCDA may become IR-active is IDCT. We note that IDCT associated with the excitation of vibrational modes implies a partial filling of the lowest unoccupied molecular orbital (LUMO) of PTCDA molecules in the top layer. According to the calculated density of states, the LUMO of these species is located a mere 0.2 eV above the Fermi level (see figure 6), whereas experiment suggests notably higher energies, which renders it entirely unoccupied [16].

It was established [52, 53] that weak coupling between a metal surface and adsorbed molecules results in a polarization of the substrate, that has a large influence on the energy level alignment. This nonlocal correlation effect can not be
can thus be given by a superposition of two spectra (i) of the PTCDA bilayer IR spectrum in the entire spectral range subject to only minor changes. A reasonable description of increased by a factor of 3.

-$P/P/Ag(1\ 1\ \ 1)$ (red line). Full spectrum (top panel), spectrum $\alpha$ second-adlayer (bottom panel). An artificial line broadening of contact layer. The accurate experimental data can help to affect the equilibrium positions of first-layer molecules quite differently, while the partly filled former LUMOs of PTCDA molecules and the Ag(1\ 1\ \ 1) substrate is quite well described by covalent interaction between a monolayer of PTCDA molecules and the Ag(1\ 1\ \ 1) substrate. Indeed, in contrast to the strongly adsorbed PTCDA/Ag(1\ 1\ \ 1) bilayer adheres to $\gamma$ stacking

Figure 7. Calculated IR-spectra of $\gamma$-$P/P/Ag(1\ 1\ \ 1)$ (black line) and $\alpha$-$P/P/Ag(1\ 1\ \ 1)$ (red line). Full spectrum (top panel), spectrum with frozen contact layer (in the middle) and spectrum with frozen second adlayer (bottom panel). An artificial line broadening of 2 cm$^{-1}$ has been applied to the calculated spectra. The intensities of the (calculated) modes with frequencies below 900 cm$^{-1}$ were increased by a factor of 3.

described properly within common DFT calculations; rather, a renormalization of Kohn–Sham molecular electronic levels is necessary [54, 55].

In our case, the second adlayer is weakly coupled to the contact layer on the metal substrate and it is likely that the DFT calculation predicts an incorrect alignment of the levels of the molecular adlayer with respect to the Fermi energy of the Ag substrate. Indeed, in contrast to the strongly adsorbed monolayer, unoccupied levels of weakly coupled molecules in the second adlayer are sensitive to slab polarization by an external electric field which exactly compensates the artificial dipole moment in slab calculations [35, 36]. As a consequence the LUMOs of molecules A and B in the second layer shift by $\sim$0.1 eV towards higher energy as clearly seen in figure 6, while the partly filled former LUMOs of PTCDA molecules in the contact layer keep their energies. Therefore aforesaid renormalization of the molecular levels (that has not explicitly been carried out in this study) will move the LUMO of second-layer PTCDA molecules higher in energy, consistent with the experimental values. Thereby, apparent IDCT effects between Ag(1\ 1\ \ 1) and the top-layer molecules are eliminated.

If this artificial IDCT effect is removed, all contributions from the in-plane vibrational modes of the molecules of the topmost organic layer vanish in the calculated IR-spectrum, in accordance with the measurements. At the same time, out-of-plane vibrational modes in the range of 600–950 cm$^{-1}$ are subject to only minor changes. A reasonable description of the PTCDA bilayer IR spectrum in the entire spectral range can thus be given by a superposition of two spectra (i) of the PTCDA/Ag(1\ 1\ \ 1) contact layer and (ii) of the free-floating PTCDA monolayer; alternatively, one may combine the full spectrum of the PTCDA/Ag(1\ 1\ \ 1) bilayer (at $\omega < 900$ cm$^{-1}$) and of the $\gamma$-$P/P/Ag(1\ 1\ \ 1)$ spectrum with frozen second layer (at $\omega > 900$ cm$^{-1}$), as has been done in figure 5.

It is worthwhile to note that despite considerably different adsorption geometries of $\gamma$ and $\alpha$-stacked bilayers on Ag(1\ 1\ \ 1) only small differences are found in the calculated IR spectra; this in particular holds for the vibrational bands at $\omega < 900$ cm$^{-1}$ which display an only weak selectivity regarding $\gamma$ and $\alpha$ discrimination (see figure 7 top panel). Worth mentioning are the enhanced splitting of first-layer PTCDA modes at about 650 cm$^{-1}$ and the multiple bands at 780–820 cm$^{-1}$ which experience an intensity gain on the high frequency side for the $\gamma$-stacked bilayer, in accordance with the experiment (see figure 4, top panel).

Upon inspection of the in-plane vibrational modes we find that both, $\gamma$- and $\alpha$-stacked bilayers suffer from the erroneously enhanced dynamic dipole moments of second-layer PTCDA species which add extra features to the calculated spectra in the top and middle panels of figure 7 (spectral region $\omega > 900$ cm$^{-1}$). This is why evaluation of the bottom panel (where the influence of the two stacking schemes on first-layer molecules is shown) is more useful. Most features at $\omega > 900$ cm$^{-1}$ are virtually identical for $\gamma$ and $\alpha$-stacked bilayers; the only exception is the characteristic C–O stretching and C–H out-of-plane bending modes react sensitively to slab polarization by an external electric field which exactly compensates the artificial dipole moment in slab calculations [35, 36]. As a consequence the LUMOs of molecules A and B in the second layer shift by $\sim$0.1 eV towards higher energy as clearly seen in figure 6, while the partly filled former LUMOs of PTCDA molecules in the contact layer keep their energies. Therefore aforesaid renormalization of the molecular levels (that has not explicitly been carried out in this study) will move the LUMO of second-layer PTCDA molecules higher in energy, consistent with the experimental values. Thereby, apparent IDCT effects between Ag(1\ 1\ \ 1) and the top-layer molecules are eliminated.

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4. Summary

The influence of the second adlayer on the structural and vibrational properties of the PTCDA/Ag(1\ 1\ \ 1) contact layer was studied by IR absorption spectroscopy in combination with density functional theory calculations. The case of strong covalent interaction between a monolayer of PTCDA molecules and the Ag(1\ 1\ \ 1) substrate is quite well described by the vdW-DFT calculations, which provide a good agreement with the experimental adsorption geometry as previously shown. In addition, the calculated fundamental vibrational modes, obtained in the harmonic approximation, together with IR-intensities derived from the dynamic dipole approach give a reasonable description of the measured IR-spectrum.

As follows from the calculations, the second adlayer affects the equilibrium positions of first-layer molecules quite noticeably, and the adsorption height depends strongly on the layer arrangement. Thereby, the change in adsorption geometry reflects itself in the IR-spectrum; especially the C–O stretching and C–H out-of-plane bending modes react sensitively, while the other ones show only small changes.

The comparison of experimental IR spectra with the computations represents a sensitive test of the weak interaction between second-layer PTCDA and the PTCDA/Ag(1\ 1\ \ 1) contact layer. The accurate experimental data can help to reveal an improper energy level alignment at the interface in
the DFT calculations as is well-known for many exchange correlation functionals. This misalignment results in artificial interface dynamical charge transfer between Ag substrate and the top-layer molecules, which in turn creates spurious bands in the IR spectrum, in contradiction to the experiment.

Clearing of the calculated IR-spectrum from these erroneous contributions provides a good agreement with the measurements.

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ORCID iDs

N L Zaitsev https://orcid.org/0000-0003-3107-7118
R Tonner https://orcid.org/0000-0002-6759-8559

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