Identifying tips for intramolecular NC-AFM imaging via *in situ* tip fingerprinting

Hongqian Sang,[1,2] Samuel P. Jarvis,[3] Zhichao Zhou,[1] Peter Sharp,[3]
Philip Moriarty,[3] Jianbo Wang,[1,*] Yu Wang,[1,†] and Lev Kantorovich[2,‡]

[1] *School of Physics and Technology, Center for Electron Microscopy and MOE Key Laboratory*
of Artificial Micro- and Nano-structures, Wuhan University, Wuhan 430072, China
[2] *Department of Physics, King's College London, The Strand, London, WC2R 2LS, U.K.*
[3] *The School of Physics and Astronomy, The University of Nottingham, Nottingham, NG7 2RD, U.K.*

I. OSCILLATION AMPLITUDE IN FM-AFM

A small oscillation amplitude offers the possibility to reconstruct the force field from a single-shot experiment and also enhances the image contrast[1,2]. To ensure the oscillation amplitude is of the same order of magnitude (only few Angstroms) as the range of the interaction, typically a relatively stiff cantilever will be used in experiment. In our simulation, the resonance frequency of the sensor is assumed to be 25 KHz and the spring constant 2000 N/m on the basis of typical measurements[3] when a widely used commercial qPlus sensor with an attached etched tungsten tip coated with silicon is employed.

In FM-AFM, the cantilever can be considered as a weakly perturbed harmonic oscillator. If the frequency shift is not large with respect to the fundamental frequency f_0 of the sensor, then the frequency shift can be obtained using equation[4]

$$\Delta f(d, k, A_0, f_0) = -\frac{1}{2\pi} \frac{f_0}{kA_0} \int\limits_0^{2\pi} F_{ts}(d + A_0 + A_0 cos\alpha)cos\alpha d\alpha \ ,$$

which depends on the operational conditions (the cantilever spring constant k and the oscillation amplitude A_0) and the distance of closest approach d. Above, $F_{ts}(z)$ is the total force acting on the tip separated by distance z from the surface.

Initially different oscillation amplitudes were tested as shown in Fig. 1. In all calculations to be described here the oscillation amplitude of the cantilever was set to 1 Å.

II. BASIS SET SUPERPOSITION ERROR ANALYSIS

A use of localized basis sets in DFT calculations of tip-sample energies/forces results in a tip-position dependent basis set superposition error (BSSE). The BSSE error increases as the tip approaches the surface, which results in an overestimation of the attractive interaction between the tip and the surface. To evaluate its impact on the calculated forces, counterpoise (CP) corrected force curves were calculated for two tips above two lattice sites and compared with force curves obtained without the BSSE correction in Fig. 2. The tip-sample interaction is relatively strong for the Si tip and the BSSE correction is negligible here. The value of the BSSE correction is noticeable when the tip-sample interaction is relatively weak, e.g. in the case of the O down NTCDI tip, and when the tip-sample distance is small. However, as follows from our calculations shown in Fig. 2, the overall shape of the force curves and their relative arrangement do not change. For instance, at tip-sample distance of 3 Å, the BSSE correction brings a corresponding force error smaller than 0.04 nN. As the calculation of the CP correction is relatively expensive, this was not done for all spectroscopy curves reported here. However, the test results for the two tips corresponding to strong and weak tip-surface interactions, as reported here, indicate that qualitative conclusions of our study should remain unchanged.

III. RAW FORCES ON SI (111)-7×7 SURFACE

In STM measurements on the Si (111)-7×7 surface, the dual-polarity bias image provides both empty and filled states of the surface, and it is possible to distinguish two halves of the unit cell due to the stacking fault in the faulted half. However, distinguishing the two halves in AFM is more challenging and is generally thought that very small structural height differences (of about 0.1 Å) would not necessarily manifest themselves in AFM, and this is generally confirmed by our simulations. In our simulations, corner adatom at faulted half (CoA-F) is somewhat more attractive than the corner adatom at the unfaulted half (CoA-U) at higher distance and less attractive at close approach except for the O-down NTCDI tip. The calculated raw forces for all ten sites including the corner hole can be found in Fig. 3.

IV. UNDERSTANDING THE INTERACTION MECHANISM AND IMAGE CONTRAST ON SI (111)-7×7 SURFACE

The strong attraction between the reactive tips and Si adatoms/rest atoms can be ascribed to the onset of covalent bonding between the dangling bonds on the Si adatoms and the tip apex. We are more interested in the functionalized chemically inert tips because strong bonding may result in manipulation of the atom or molecule on surface and/or tip modification which would make analysing the imaging very difficult.

On the Si(111)-7×7 surface, the distribution of the electrostatic potential does not follow exactly the topography, see the bottom image in Fig. 2 of the main text. In our simulations, a contrast inversion is observed for adatoms and rest atoms in the image when using the H-down NTCDI tip as well as for other negatively charged tips. It seems that similar contrast inversion was observed by Kelvin probe force microscopy (KPFM) measurements[5]. These results clearly demonstrate the capability of the polar molecule to serve as an AFM probe by atomically resolving potential distribution. Moreover, we show that the sign of the electrostatic potential at the tip apex can be identified by comparing the forces measured above the adatom and rest atom sites.

Further investigation of the interaction mechanism requires looking at the electron distribution in the tip-surface junction in detail. As an example, let us consider the interaction between the NTCDI tip and the adatoms and rest atoms of the Si surface. To this end, the electron density difference (EDD) obtained by subtracting the densities of the isolated tips and surface from the relaxed total density of the full system, appears to be very useful and informative. The EDD describes the electron redistribution caused by the presence of the tip and can be calculated at a number of tips heights and locations. The EDD is plotted in Fig. 4 at heights of $z =$3.0 and 3.5 Å for both tip orientations above the adatom (a,c) and the rest atom (b,d) sites. The electron redistribution above adatoms and rest atoms is associated with the electrostatic potential field below the tip apex, see Fig. 3(f) of the main text. The H-down NTCDI tip produces a positive potential which attracts the electron cloud when approaching the adatom (the upper left images), while the O-down tip, which produces a negative electrostatic potential, has an opposite effect above the same site. In the case of the rest atom, only a small excess of the electron cloud for the H-down tip is observed, while the effect of the expulsion of the electron density for the O-down tip is much stronger than in the case of the adatom.

We also considered the possibility that the larger interaction of the H-down NTCDI tip above the rest atom site may in fact be due to the side oxygen groups interacting with the surrounding surface. To clarify the possible influence of the side groups, a new tip, formed by the H-down isoindole molecule, was tried for comparison. The H-down isoindole also produces a positive electrostatic potential but has no side groups near the apex, see right inset in Fig. 5. As seen in Fig. 5 the force curves calculated for isoindole produce very similar results - with the same ordering of the maximum attractive force above the adatoms and restatoms - as compared to the H-down NTCDI tip. As such we conclude that side groups do not influence the contrast at the heights investigated.

V. FORCES AND FREQUENCY SHIFTS SIMULATED ON NTCDI MOLECULE ADSORBED ON AG:SI(111)-$(\sqrt{3} \times \sqrt{3})R30°$ SURFACE

Forces over different sites on chemically inert NTCDI molecule adsorbed on Ag:Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$ surface are sensitive to the electrostatic potential of the tip apex. In addtition to the C-C and hexagon centre sites discussed in the main text, two more sites were considered in our simulations when using the NTCDI tips: the O atom (site C) and H atom (site D) of the molecule as shown in Fig. 6, where the electrostatic potential is the lowest and highest, respectively.

The tip forces and detuning frequencies calculated for all our eight tip models above the sites of the molecule are shown in Fig. 7. The maximum attractive force for the H-down NTCDI tip is 0.38 nN above the O atom sites, while for the O-down NTCDI tip the maximum attractive force is 0.21 nN above the H atom sites. These results show that it must be possible to map the distribution of charge on the surface by NC-AFM using differently orientated polar molecular tips without applying voltage between tip and surface as it is done in KPFM.

---

[*] wang@whu.edu.cn(JW)

[†] yu.wang@whu.edu.cn(YW)

[‡] lev.kantorovitch@kcl.ac.uk(LK)

[1] Giessibl, F. J., Hembacher, S., Bielefeldt, H. & Mannhart, J. Subatomic Features on the Silicon (111)-(7×7) Surface Observed by Atomic Force Microscopy. *Science* **289**, 422–425 (2000).

[2] Majzik, Z. *et al.* Room temperature discrimination of adsorbed molecules and attachment sites on the Si(111)-7×7 surface using a qPlus sensor. *ACS Nano* **7**, 2686–2692 (2013).

[3] Weymouth, A. J., Wutscher, T., Welker, J., Hofmann, T. & Giessibl, F. J. Phantom force induced by tunneling current: a characterization on Si(111). *Phys. Rev. Lett.* **106**, 226801 (2011).

[4] Garcia, R. & Pérez, R. Dynamic atomic force microscopy methods. *Surf. Sci. Rep.* **47**, 197–301 (2002).

[5] Fujikawa, Y., Nakajima, K. & Sakurai, T. (eds.) *Frontiers in Materials Research (Advances in Materials Research)* (Springer, 2008), 2008 edn.
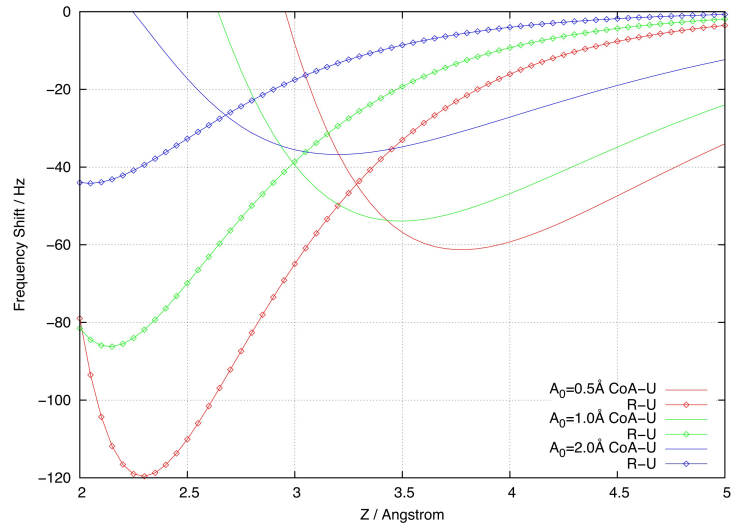
FIG. 1. Frequency shift versus the distance of closest approach. Si tip in H3 configuration approaches the adatom (solid line) and rest atom sites (solid line marked with square) on Si(111)-7×7. The tried oscillation amplitudes of the cantilever are: 0.5 Å (red), 1 Å (green) or 2 Å (blue).
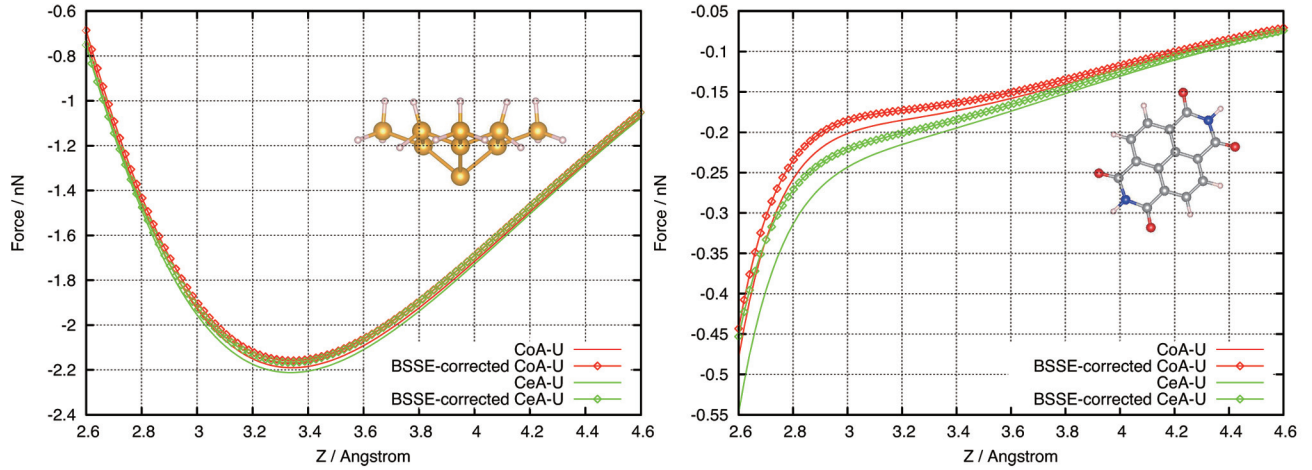

FIG. 2. Tip force versus distance curves for Si tip in H3 configuration (on the left) and O down NTCDI tip (on the right) approaching the corner adatom (red) and centre adatom (green) sites on the Si(111)-7×7 surface. Counterpoise corrected force curves are marked with squares.
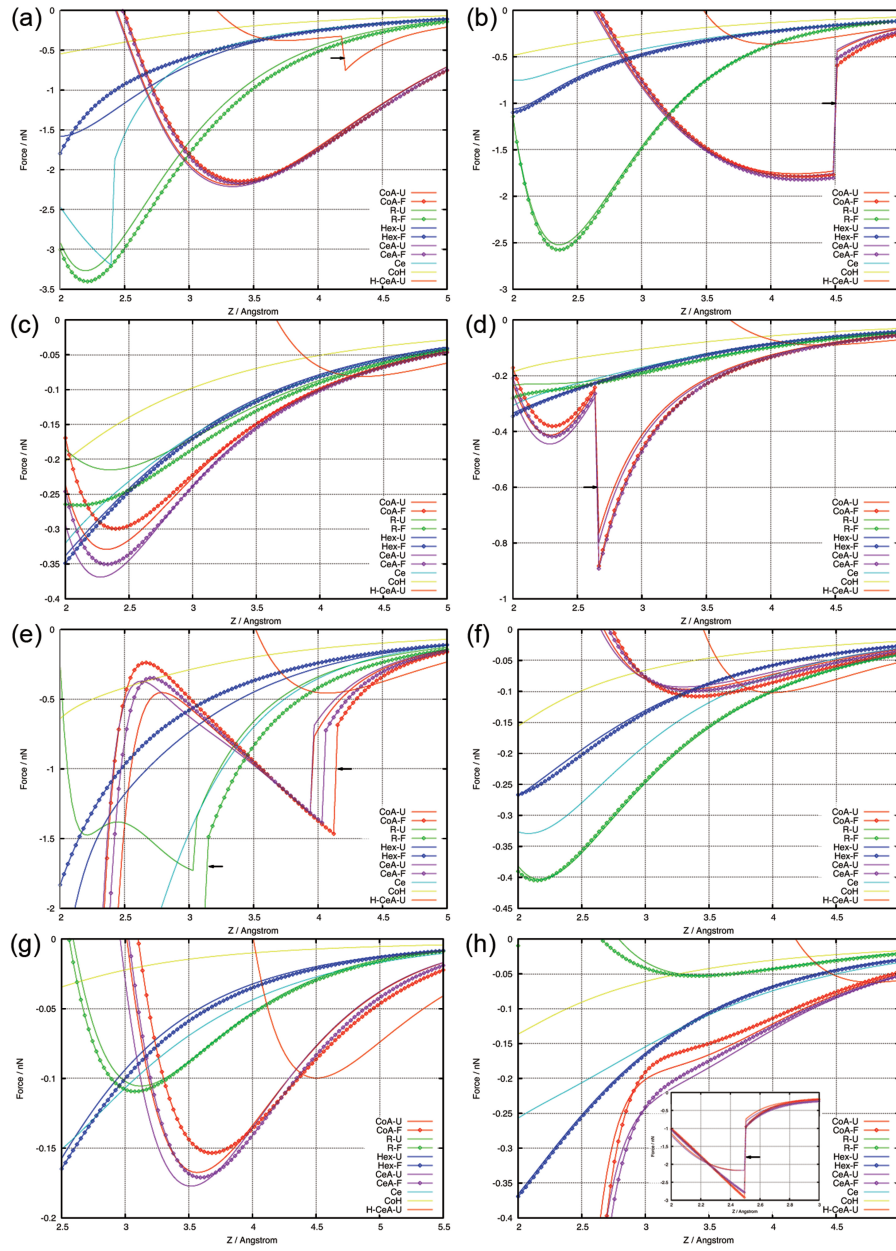
FIG. 3. Tip force versus distance curves for all tip candidates approaching selected sites on the faulted (solid line) and unfaulted (solid line marked with squares) halves of Si(111)-7×7. Different colours represent different lattice sites as indicated. Tips in (a) to (h) correspond to the models in Fig. 4 in the main text.
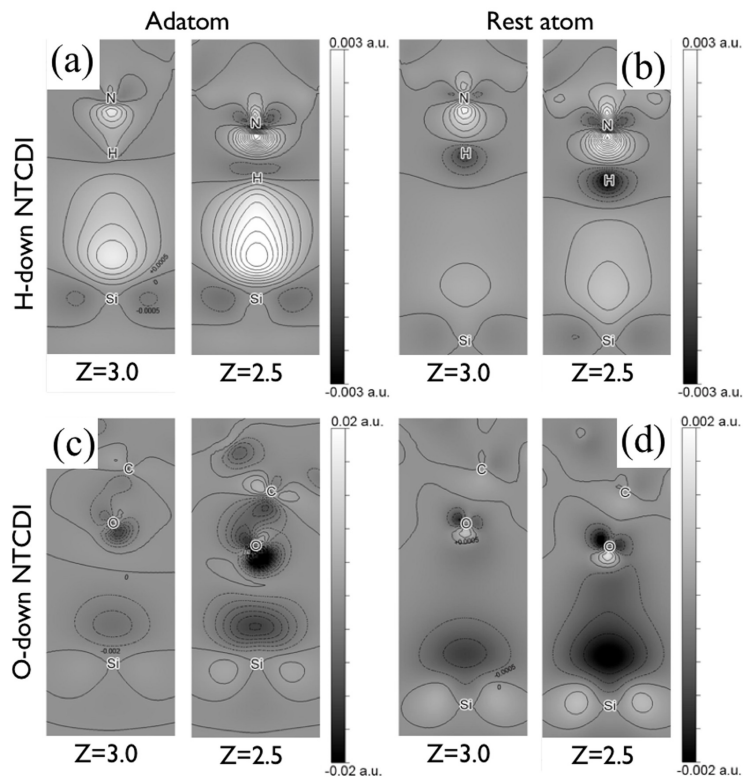
FIG. 4. Evolution of the electronic density difference (EDD) for the NTCDI tip in the H-down (a,b) and O-down (c,d) orientations approaching the adatom (a,c) and rest atom (b,d) sites on the Si(111)-7×7 surface. Positive values of the EDD (white regions) correspond to excess, while negative (dark) to expulsion of the electron density.
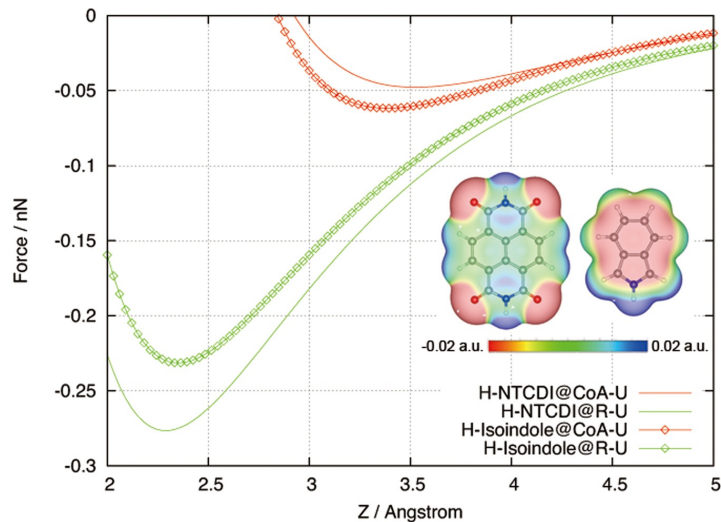

FIG. 5. Comparison of the force versus distance curves of H-down NTCDI and H-down isoindole molecule approaching the adatom and the rest atom sites on Si(111)-7×7. Inset: H-down NTCDA (on the left) and the isoindole (on the right) molecules.
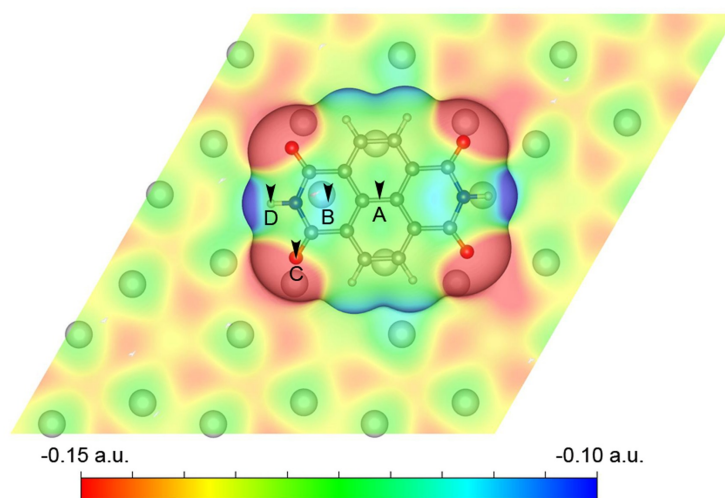
FIG. 6. The EPS of a single NTCDI molecule adsorbed on Ag:Si surface. Only the NTCDI molecule and Ag atoms on the upper surface layer are visualized. The black arrows labeled with A, B, C and D indicate the C-C bond at the centre of the molecule, the centre of a C_5N hexagon, the O atom and the H atom (bonded with N atom), respectively.
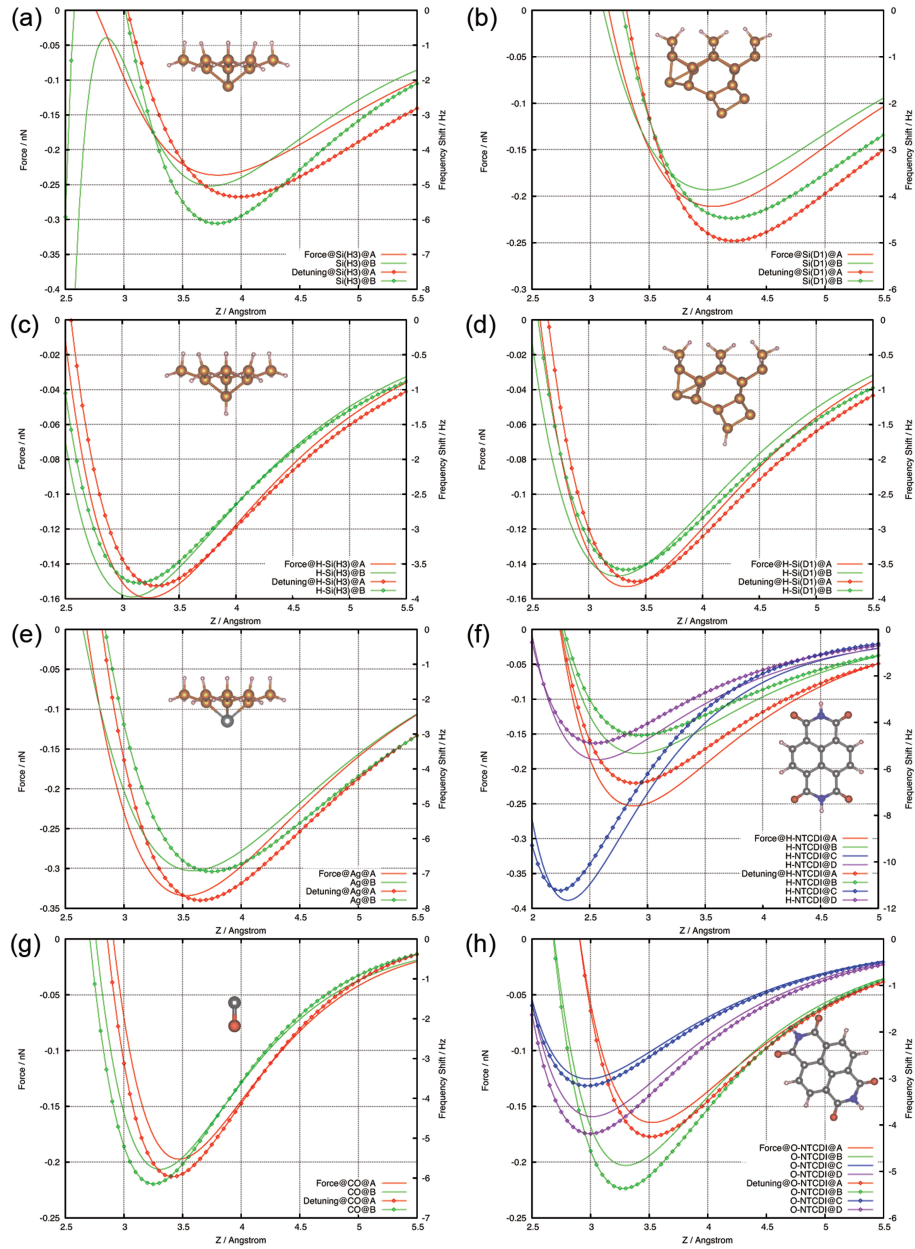
FIG. 7. Tip force (solid line) and detuning frequency (solid line marked with squares) versus distance curves for different tips approaching the C-C bond at the centre of the molecule (red), the centre of a C_5N hexagon (green), the O atom (blue) and the H atom (purple).