Atomistic Design of Quantum Biomimetic Electronic Nose

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***Abstract*— Understanding the enigmatic mechanism of olfaction from a biomimetic technology perspective would be very useful for electronic nose applications. The inelastic tunneling spectroscopy (IETS) of various odorant-receptor systems are simulated for this purpose. An atomistic simulation framework is presented for the same. Analysis of the results offer an insight into how an actual biomimetic sensor system can be made to detect incoming odorant molecules.**

Keywords—biomimetic, IETS, electronic nose, vibration theory of olfaction

I. INTRODUCTION

The ability of the biological nose in able to distinguish between numerous types of smells is one of the important reasons of survival. There is a dire need and interest in modeling the sensation of smell in our noses into a physical sensor with as many degrees of freedom as a real biological nose would have. The applications and advantages of such a sensor is numerous: in clinical diagnosis, industries and defense, to name a few.

For this, it is first essential to understand the theory behind the sensation of olfaction, which is still not clear fully, as a single explanation has not yet been worked out. The shape theory puts forth one picture, in which the physical shape of the odorant chemical acts as a "key", fitting into the corresponding receptor in our noses that locks into it [1]. The signals triggered by receptors are interpreted by our brains. However, it has been seen that molecules having radically different structures have similar odors, and molecules having very similar shapes (with minor differences in the structure) have very different smells. Clearly, this is not explained by the shape theory.

The vibration theory of olfaction proposes that when odorants bind with olfactory receptors, the molecular vibrations are detected [2]. This theory was expanded to incorporate a detailed quantum mechanical (inelastic tunneling) based approach [2] as a plausible mechanism for our sense of smell. While evidence has emerged in the favor of vibrational theory over the years, there also has been contradictions. The swipe card model [3] is a possible alternative model which combines the shape and vibration theory. It proposes that firstly, the shape of the odorant molecule has to be good enough to fit the receptor, and secondly, additional information is conveyed when an inelastic tunneling channel is opened up between the receptor contacts, corresponding to its specific vibrational energy, which helps in the detection of the odorant molecule.

We try to probe further into the mechanism of olfaction through an atomistic simulation framework for the design of electronic nose sensors that are biomimetic in the sense of the vibration theory, as shown in Fig. 1. This is done by analyzing the inelastic tunneling spectroscopy (IETS) [4] for odorant molecules. IETS comprises of peaks in the second derivative of the I-V characteristics of a tunneling barrier. It shall be shown that these peaks correspond to the vibrational modes in the tunneling path.

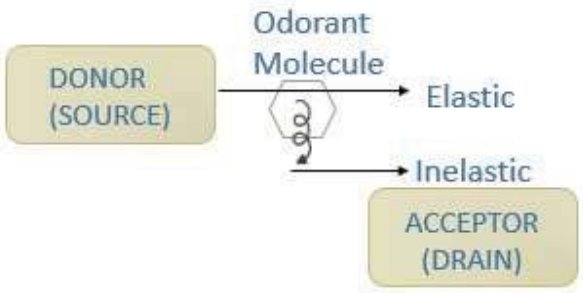


Fig. 1. Schematic of a simplified model of an olfaction sensor based on Turin's proposed mechanism. The Donor and Acceptor are embedded on the receptor junction. Electrons are able to tunnel through inelastically from donor to acceptor by exciting vibrational modes of appropriate energies when an odorant molecule occupies the binding site.

II. SIMULATION METHODOLOGY

For atomistic scale simulation of molecular configurations, the software ATK-VNL, from QuantumWise, has been used [5]. For calculation of electronic structure, transport properties, electron-phonon couplings, IETS, vibrational modes and frequencies, of a device placed between two metallic electrodes under non-equilibrium conditions, ATK-VNL uses methods of first principles, DFT, or tight binding semi empirical methods, like Slater Koster, for electronic structure calculations.

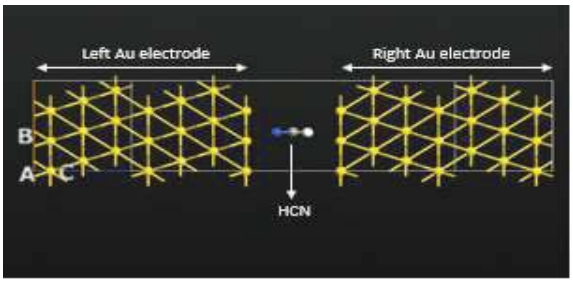
Before doing any electronic structure or transport calculations, it is necessary to ensure that the molecular junction device has been appropriately built and optimized. For IETS calculations, information from the dynamical matrix and the Hamiltonian derivatives matrix is required [6]. Dynamical matrix is defined in terms of interatomic force constants that are used in the displacement of atoms back and forth in each spatial direction. The elements are defined as:

$$D_{\mu\alpha,\iota\beta} = \frac{dF_{\iota\beta}}{dr_{\mu\alpha}} \quad (1)$$

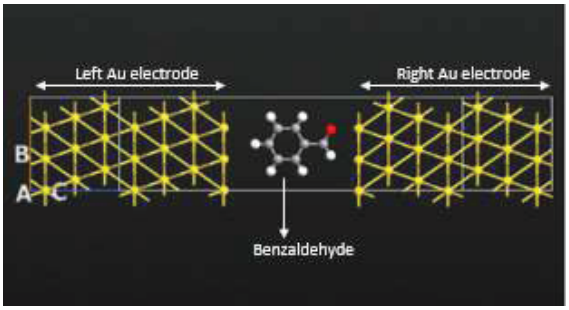
Where $F_{\iota\beta}$ is the force on the ιth atom in the direction β, and r denotes the displacement of the μth atom displacing in the direction α. The phonon self-energies are obtained from the electron-phonon (e-ph) coupling matrix M^{λ} for a particular phonon mode λ, which is obtained by expanding the tight-binding Hamiltonian to first order in the atomic displacements. The couplings are expressed in terms of derivatives of Hamiltonians and overlap matrices. Lowest order expansion (LOE) method is chosen to simplify the integrals over energy in the calculation of self-consistent Born approximation (SCBA) electron-phonon energies.

A. HCN and Benzaldehyde

If molecular vibrations are indeed part of olfactory mechanism, there should be some similarities between odorants which possess similar smells, which we hypothesize should be visible in their IET spectrum. Taking the example of two simple molecules from the bitter-almond odor descriptor family, hydrogen cyanide (HCN) and benzaldehyde, IETS simulation is carried out. The corresponding two-probe device configuration is shown in Fig. 2, with the vibrational modes being introduced by the odorant in between the two electrodes, which correspond to the receptor. The electronic structure of the system is calculated through semi-empirical Slater-Koster tight-binding method.



(a)



(b)

Fig. 2. Two-probe atomistic device sensor configuration, based on Fig. 1, for transport through (a) Hydrogen Cyanide (HCN) and (b) Benzaldehyde, which are the odorant molecules between left (Donor) and right (Acceptor) Gold electrodes.

B. Resonant Tunneling Diode (RTD)

Experimentally, IETS measurements, traditionally carried out in metal-insulator-metal devices, need cryogenic temperatures to preclude thermal broadening of the peaks. If inelastic tunneling is indeed the mechanism behind biological olfaction, IETS must take place at ambient temperatures at least. Attempts are made to reduce the thermal broadening of peaks using energy filters, and the effectiveness of usage of a resonant tunneling diode has been shown in [7]. The schematic of such a sensor system, incorporating RTD, is as shown in Fig. 3.

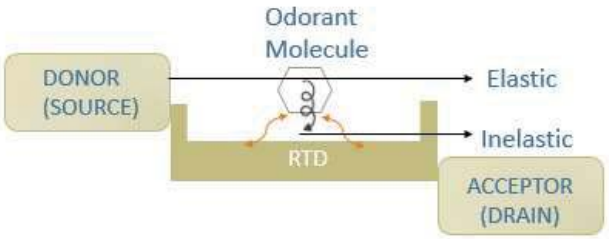


Fig. 3. Schematic of a proposed model of a more efficient olfaction sensor. The sensor system consists of the donor, acceptor and a double-barrier resonant tunneling diode (RTD), which can be used as an effective energy filter to achieve higher temperature operation.

For atomistic simulation purposes, a molecular structure showing RTD characteristics [8] is used for probing IETS. The two-probe configuration for IETS simulations is shown in Fig. 4.

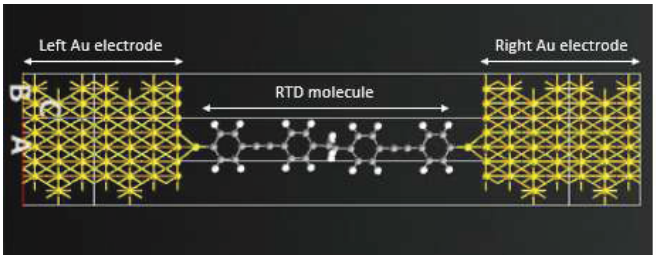
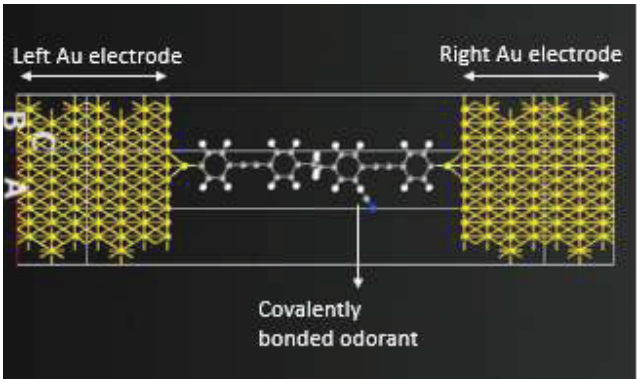


Fig. 4. Two-probe atomistic device sensor configuration, based on Fig. 2. The specific molecular chain introduced in between the left and right electrodes gives the characteristics of a resonant tunneling diode (RTD) [Perrin's paper]. This entire system is our proposed sensor for odorant molecules.

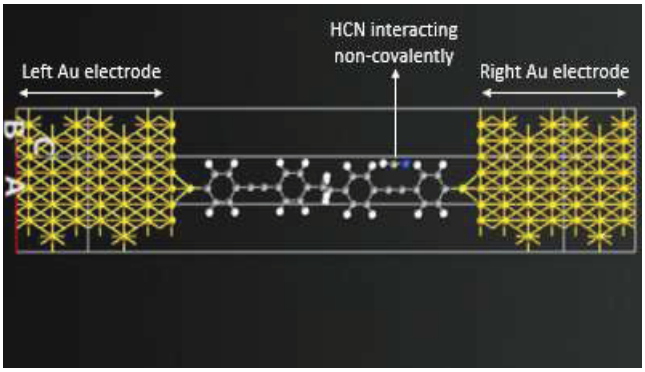
C. RTD with Odorant Molecules

Considering the base sensor configuration as shown in Fig. 4, odorant molecules are brought in and the effect on the IETS of the whole system is observed. The odorant molecule considered is hydrogen cyanide, HCN, for a simple starting case. There are two ways in which HCN can interact with the sensor system: being covalently bonded or non-covalent interactions. One of the possible configurations of HCN being covalently bonded to the sensor system in shown in Fig. 5 (a), where one of the H-atoms of the molecular RTD is replaced by CN^- ion. One of the possible configurations of HCN interacting non-

covalently with the sensor system is shown in Fig. 5 (b). There are also numerous other configurations possible, depending on how the odorant system comes in.



(a)



(b)

Fig. 5. The possible ways in which odorant (HCN) interaction with the proposed sensor system can be modeled. (a) Through covalent interactions, in which CN^- ion from HCN is substituted by replacing an H-atom from the system, (b) Through non-covalent interactions, in which HCN molecule interacts with the system at a distance.

IETS simulations are done for both the configurations shown in Fig. 5 the usual way, and the results are compared.

III. RESULTS & DISCUSSION

The IETS simulation results for HCN and benzaldehyde, the odorant molecules shown in Fig. 2, are compared and shown in Fig 6.

There is a clear overlap in the IETS peaks observed at 61.9 mV. We therefore conjecture that this peak leads to the characteristic bitter-almond smell for both of these odorants.

The eigenvalues of the dynamical matrix yield the squares of the vibrational frequencies, from which the vibrational energies can be calculated. The vibrational modes for HCN and the corresponding closest values for benzaldehyde are noted in Table 1. It can be seen that the vibrational mode energies have a one to one correspondence with the IETS peaks.

TABLE I. VIBRATIONAL MODE ENERGIES

HCN (in meV)	Benzaldeyde (in meV)
7.86	7.37
31.79	24.85
61.9	61.98
63.39	72.15
242.21	193.96
446.77	428.68

The IETS for odorant-sensor system configurations of Fig. 5 are simulated, and the results are compared in Fig. 7. Apart from the observation of correspondence of vibrational mode energies with IETS peaks, it may be noted that for the dominant peaks, the non-covalently bonded HCN-sensor system (Fig. 5 (a)) nearly matches with the HCN- sensor system of Fig. 2 (a). This indicates that, as might be intuitively expected, olfaction corresponds to physical adsorption of odorant molecules; this in turn is therefore what we should aim to emulate in sensing.

The results suggest the possibility of atomistic design of electronic nose sensors inspired by the vibration theory of biological olfaction. Extensive calculations, and validation experiments, will be needed to make this a reality.

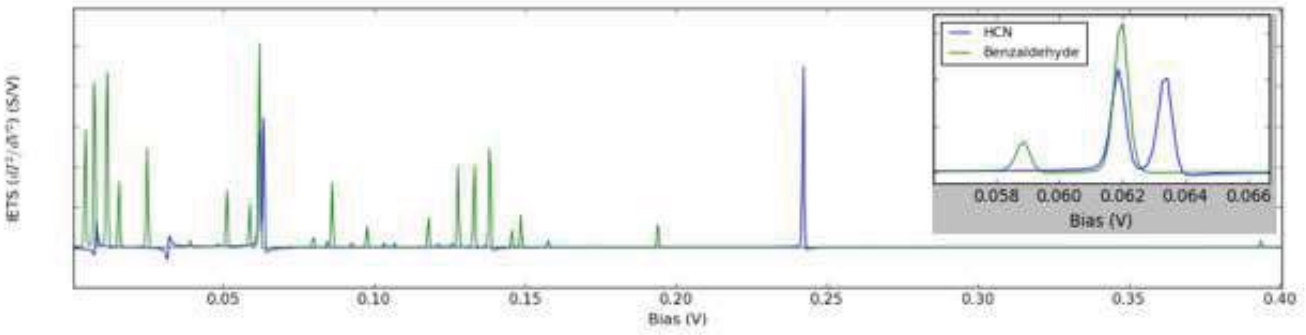


Fig. 6. Comparison of normalized IET spectra for HCN (Blue curve) and Benzaldehyde (Green curve) at 1 K, calculated by lowest-order expansion (LOE) approximation. (a) is for a bias from 0 to 0.4V, (b) is a zoomed-in view, clearly showing the matching of the IETS peak at 0.061V.

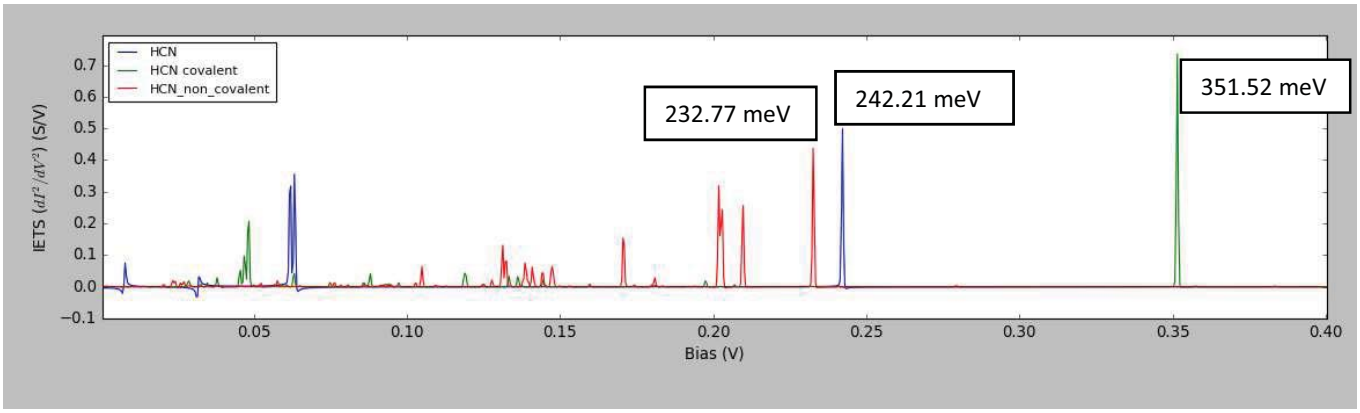


Fig. 7. Comparison of normalized IET spectra for (a) Just HCN in the sensor configuration of Fig. 3(a) (blue curve), (b) HCN covalently bonded to RTD molecule in sensor configuration of Fig. 7(a) (green curve) and (c) HCN interacting non-covalently with the sensor system of Fig. 7(b) (red curve). The corresponding vibrational mode energies are indicated. It is observed (a)'s peak at 0.232V and (c)'s peak at 0.242V nearly match.

IV. Acknowledgement

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V. References

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