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In Situ Raman Spectra of a Conical Conductive Shell as an Electro Galvanic Spin Orbit Transformer (SPOT)

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Abstract

Experimental results are interpreted, which were obtained by tip enhanced Raman Spectroscopy (TERS) in a specific SNOM (Scanning Near-Field Optical Microscope) STM (Scanning Tunneling Microscope) configuration with a tunnel gap. The interpretation is performed in terms of a classical physical model of a photon as a vacuum phonon polariton. The metal tip is considered as a conductive infinitely thin shell of a diamagnetic electron gas. The stationary single electron tunnel current \( I = e f_{\text{tunnel}} \) of an electron tunnel passage frequency \( f_{\text{tunnel}} \) carries not the charge \( e \) but is shown to carry an energy \( h f_e \) and an isotropic orbital angular momentum \( \frac{h}{4\pi} \) which corresponds to an isotropic transversal electron spin density of an angular frequency \( 2\pi^2 f_e \). The electron spin current corresponds to an isotropic azimuthal inertial torque which acts on the photon by an increase of its energy and torque. Neglecting the influence of thermal and radiative losses of the conductive shell, the interpretation reproduces the spectroscopic results within the uncertainty of the experimental results. The photoelectric Raman spectrum of the tunnel gap can be regarded as a
complex admittance spectrum which depends in a nonlinear way on the tunnel voltage, the tunnel current and the wavelength of the scattered light. The conical tunnel gap configuration can be considered as a bipolar Electro-Galvanic Spin-Orbit Transformer (SPOT) and from a thermodynamic viewpoint as a Quantum Energy Converter

**Keywords:** Raman Spectroscopy, Electron Spin, Photon Spin, relativistic Quantum mechanics

**Introduction**

Experimental results are interpreted, which were obtained by tip enhanced Raman Spectroscopy (TERS) in a specific SNOM (Scanning Near-Field Optical Microscope)-STM (Scanning Tunneling Microscope) configuration with a tunnel gap between a gold coated glass tip and a thin film of gold.

**Experimental Configuration**

A corner of a glass fragment which is coated with a 20-50 nm thick film of gold is used as a tip for STM (scanning tunneling microscopy) and TERS (Tip Enhanced Raman Spectroscopy) [1]. Such glass fragments have sharp edges with a radius of curvature in the order of 5 nm. This is well known from the use of glass wedges as knives for ultramicrotomy of samples for transmission electron microscopy, where slices of a thickness in the order of 30 nm are required. The glass wedges are produced by repetitive cleaving of a glass slab of a rectangular cross section. The corner of the wedge has an opening angle close to 90° and can thus be considered as the apex of a regular tetrahedron. Therefore, the tip is called a tetrahedral tip or a T-tip. As shown in Fig.1, a p-polarized coherent 633 nm photon beam, which is emitted from a He Ne Laser is normally incident into the T-tip. The coherent beam of light is considered as a coherent propagating Gaussian beam of photons and
electromagnetic radiation of a numerical aperture in the order of 0.05. This beam is retroreflected in the T-tip. The sample consists of a ca. 25 nm thick film of gold which is coated with a 4-4-bipyridine monolayer. The light, which is forward scattered from the tip through the sample is collected by an oil immersion objective lens and the spectrum of the light, which is scattered from the apex of the tip in the focus of the of the objective lens is recorded.

**Experimental Results**

Energy loss spectra are shown in Fig.2 of photons scattered through the gold film as a function of the tunnel current with a constant applied voltage of 0.1V [2]. The spectra exhibit narrow lines of the adsorbed molecules on a broad background. The redshift of the maximum with respect to the laser line decreases with increasing tunnel current. Here we focus our interest on this background. The bars indicate the position of the maximum of the background as calculated on the based on the interpretation presented here A broad band background is well known from previous TERS experiments with a TERS – STM configuration [3] and from surface enhanced elastic scattering experiments [4] with pairs of metal nanoparticles as a medium for surface enhanced scattering spectra (SES). In both cases the redshift of the maximum increases with decreasing gap distance between tip and sample (TERS) or between the nanoparticles (SES) respectively. In the SES case, however, the redshift starts was shown to decrease significantly with decreasing gap width, when the gap width reaches the 0,1 nm range where an optically induced electron tunnel process occurs which strongly influences the coupling of the particle plasmon resonances. In our case, the increase in the tunnel current is accompanied with a decrease in the gap distance due to the STM constant current to distance feedback.
Fig 1 Scheme of the experimental TERS configuration with a tetrahedral tip of glass which is coated with a thin film of gold serving as a tip.

Fig. 2 Inelastic scattering spectra. The Intensity drifted between recording of the spectra. The spectra are adjusted such, that the form of the wide band background can be compared well.
Interpretation of the Experimental Results

We interprete the Raman spectra of the tunnel gap in terms of the concept of a Fano Resonance [5] due to a coupling between a continuum of energy states and a discrete energy state which overlaps with the continuum. We define the discrete energy state as a photon of an energy corresponding to a wavelength of 633 nm. The continuum is the continuum of states of the wavefunctions of the conduction electrons. The coupling of the photons with the electrons occurs in the collision of the propagating photon with the conduction electrons in the photon reflection process. This interaction between photons and electrons has to be distinguished from radiative properties of overlapping electronic energy states which is often used to explain energy shifts due to the coupling of particle plasmon-polaritons or the coupling between plasmon-polaritons and excitons. These coupled plasmon-exciton resonances are often considered as Fano resonances but they can equally well be considered as classical electromagnetic interference phenomena [6].

Model of the Photon as an entangled Vacuum Phonon-Polariton

In the interpretation of the Raman scattering of a photon and an electron tunnel junction we cannot consider the photon as a purely electromagnetic phenomenon because a transfer of angular momentum of mechanic origin occurs in the Raman scattering process [7]. The relativistic inertial and gravitational aspects of the interacting quanta- photons and electrons without and with a rest mass respectively - have to be considered. This is done by considering the photon beam as a current of entangled vacuum phonon polaritons [8]. The model of the photon as an entangled phonon-polariton can be described in the framework of a unified theory of electromagnetism and gravitation by Bernhard Riemann [8,9]. The propagating phonon polaritons carry an energy $hf$, the phonon component carries a right handed
longitudinal spin angular momentum $\frac{h}{2\pi}$ and an inertial torque $\frac{hc}{2\pi\lambda}$ which points into the direction of propagation and is oriented along the axis of polarization. The polariton component carries a transverse torque

$$w = \frac{hc}{2\pi\lambda} = \frac{hc}{2\pi\lambda}; \frac{\partial w}{\partial \theta} = \frac{w}{2\pi}$$

These are the properties of the photon which we use for an interpretation of the experimental results on the Raman scattering of a tunnel gap without a tunnel current. The model of the photon as a vacuum phonon polariton is consistent with the electromagnetic and relativistic properties of the photon which were ascribed to the photon by P.A.M. Dirac in the framework of his relativistic quantum mechanics [10]. Dirac describes the radiative properties of a photon as properties which are linked to the transverse electromagnetic radiation which is emitted in the electric dipole transition of an electronically excited state of an atom to its ground state with the transition dipole moment oriented in the longitudinal direction. The rotationally symmetric electromagnetic radiation in the transverse direction is linearly polarized and can be considered as a superposition of left hand and right hand circularly polarized radiation propagating in a forward and backward longitudinal direction respectively. The spin angular momentum of the photon was not directly deduced by Dirac from the electromagnetic properties of the photon but by assuming a conservation of angular momentum in the radiative transitions between the ground state and the electronically excited state of the atom. The longitudinally oriented angular momentum of the excited state of the atom is transferred to the emitted photon during the transition of the dipolar excited state of the atom to the ground state, which carries no angular momentum. The emitted photon carries an angular momentum $+\frac{h}{2\pi}$ which is oriented in the longitudinal emissive forward direction. A
time inverted emission process leads to a right hand circularly polarized photon with respect to the forward directed longitudinal axis or to left hand circular polarization with respect to the backward oriented longitudinal axis of propagation. This explanation of the properties of the electromagnetic and relativistic properties of photons emitted in the decay of an electronically excited state is also in accord with the classical description of the properties of radiation emitted in an atomic transition by Sommerfeld [11]. As the forward direction is associated to the direction of emission of the photon, the emitted photon has to be left hand circularly polarized and carries a right handed angular momentum $\frac{h}{2\pi}$ in the longitudinal component of the direction of propagation of the emitted photon. We therefore conclude that the photons of a propagating polarized beam of light always carry a right-handed angular momentum with respect to the direction of propagation. Dirac’s definition of the polarization and the angular momentum of a photon was the theoretical basis for the interpretation of inelastic molecular scattering spectra involving the transition of rotational modes which led to C. Raman to the experimental derivation of the spin of the photon [7]. In the framework of this interpretation of the spin of the photon one must assume that left and right hand polarized confined beams of photons carry the same right-handed angular momentum with respect to their direction of propagation. Our model of the photon as a vacuum phonon polariton leads to the same conclusion. This view of the angular momentum of circularly polarized propagating beams of light contradicts the widely accepted view that circularly polarized confined beams of light with opposite turning sense carry angular momenta of opposite turning sense [7,12]. The additional property of the torque of a propagating photon in our model of the photon as a phonon polariton can be derived from the spin of the photon, as the time derivative of a propagating photon’s spin-angular momentum
corresponds to an inertial torque. The following interpretation is based on our classical physical model of a photon as a vacuum phonon polariton and assuming a quantized elementary charge $e$ of the electron. Our model of the photon as a vacuum phonon polariton is not consistent with quantum electrodynamics, where the existence of photon spin angular momentum has no intrinsic theoretical justification but is just imposed in order that the theory is consistent with Dirac’s relativistic quantum theory of the electron.

**Interpretation of the Raman spectra of the tunnel gap in the absence of a stationary tunnel current**

For the interpretation we neglect ohmic losses in the metal coating and we do not take into account the influence of a random thermal motion of electrons on the spectra. As shown schematically in fig. 1, a normally incident photon is retroflected in 2 reflection steps and the spin, which is oriented parallel to the axis of polarization, is inverted as it rotates by an angle $\frac{\pi}{2}$ around the transverse axis in each of the two reflection steps. Due to conservation of angular momentum, an angular momentum is transferred to the tetrahedral tip, The torque of the photon acts on the conduction electrons and therefore energy is transferred to the electrons corresponding to a decrease in energy and wavenumber of the photon: using eq (1) we obtain for the redshift

$$h\Delta f = -2\frac{\pi}{2} \frac{dW_{photon}}{d\theta}; \Rightarrow h\Delta f = \frac{hc}{4\pi} \Delta_\perp \left(\frac{1}{\lambda}\right) \Rightarrow \Delta_\perp \left(\frac{1}{\lambda}\right) = 1257\text{cm}^{-1} \ (2)$$

In this way we have determined the redshift of the energy loss spectrum in the absence of a stationary tunnel current. The position of the calculated redshift is indicated in Fig.2 by a broken line. The position is close to the maximum of the broad band background for the case of a tunnel current of 0.1 nA.
The torque of a tunnel current through a tunnel gap.

In the stationary state, the power density of the tunnel current is time and space invariant.

\[
\frac{d\mathcal{J}}{dx^3} = -j \left[ \frac{AV}{m^3} \right] \quad (3)
\]

Energy is transferred with the tunnel current from the T-tip into the sample. No energy is dissipated to heat in the vacuum tunnel gap since the vacuum has no Ohmic resistance. It is known from experiments with scanning tunneling microscopes that a gold tunnel gap can withstand a current of 1mA without a significant alteration of the gold structure. A current density is associated to such a tunnel current which would lead in the matter bound current of a metal wire to an immediate evaporation of the metal. The tunnel current \( I_{tunnel} \) can be considered as the passage of electronic charges \( e \) at a frequency \( f_e = Ns^{-1} \) through the tunnel gap:

\[
I_{tunnel} = e f_e \quad (4)
\]

If we neglect Ohmic losses in the metal shell, the velocity of the motion of electrons is space invariant and corresponds to a uniform drift velocity of the electrons. Since energy is conserved in the passage of the electrons through the tunnel gap, no energy is dissipated into heat, therefore, the kinetic energy of the electrons in the metal coating of the tip and sample is space invariant. In the passage of the electron through the tunnel gap, the tunneling electron gains, due to the electric field and the voltage difference across the tunnel gap, a stationary potential energy \( E_{pot} \)

\[
E_{pot} = \frac{1}{2} e V_{tunnel}^2 \quad (5)
\]
Since the electronic charge related to the tunnel current appears on the metal shell of
the tip as a monopolar charge \( e \) of a dipolar surface charge, we may consider the
tunnel current as a flux of dipolar electric energy through the tunnel gap. The
stationary flux leads to a stationary linear dipole moment \( p = -q_e d \), which is
determined by the distance of the tunnel gap \( d \) and the dipolar surface charge \( q_e \).
This leads to an alternative expression of the energy content of the tunnel gap as an
electric dipolar energy \( P_e \) in terms of the tunnel distance and the surface charge
\[
P_e = q_e^2 d^2 \quad (6)
\]
Since we derived the dipole from the model, that the stationary single electron tunnel
current is equivalent to the rotation of an electric dipole around a transverse axis by a
polar angle \( \theta = 2\pi \), the potential energy (5) and the dipole energy (6) have to be the
same. From this equality we can derive the tunnel distance as a function of the
surface charge \( q_e \)
\[
\Rightarrow d = \frac{V}{q_e N} \quad (7)
\]
The dipolar surface charge can be derived from the spatial continuity of the surface
charge for the case of the ideally conducting metal films, which is assumed in our
interpretation. The stationary surface charge density is determined by the stationary
tunnel current \( I_{tunnel} \) and the transverse cross sectional area \( \mathcal{F} \) of the tetrahedral tip
which, for our specific configuration (see Fig. 1) is an equilateral triangle of a base
length \( 2\rho \). For an equilateral triangle of a base length \( 2\rho \)
\[
\mathcal{F}(\rho) = \rho^2
\]
\[
\Rightarrow q_e(\rho) = \frac{N}{\frac{\rho}{2}} e \quad (8)
\]
\[ P_{el} = q_e^2 d^2 = \frac{N^2}{4} e^2 d^2 = \frac{1}{2} eV^2 (9) \]

This relation leads to a quantitative functional relation between the tunnel gap distance \( d \) as a function of the tunnel frequency \( f_e \) for a given tunnel voltage \( V \).

\[ d = \frac{V}{f_e} \sqrt{\frac{2}{e}} (10) \]

In a similar way we can define an electronic surface mass

\[ q_{me} = \frac{N}{2} m_{el} (11) \]

As indicated in Fig. 1, in our specific configuration the longitudinal cross section of the tetrahedral tip is an equilateral rectangular triangle of the height \( \rho \) and we obtain for the volume \( Vol \)

\[ Vol = \frac{\rho^3}{2} (12) \]

Therefore, we obtain for the electron charge density \( q_{charge} \) in the volume of the tetrahedral tip

\[ q_{charge}(\rho) = \frac{Ne}{\rho^3} = \frac{Ne}{\rho^3} (13) \]

and for the surface charge density

\[ q_{charge}(\rho) = \frac{Ne}{2\rho^2} (14) \]

and for the surface mass density

\[ q_{mass}(\rho) = \frac{Nm_{el}}{2\rho^2} (15) \]
The electron surface density has a singularity in the center of the tunnel gap at the extrapolated apex of the tetrahedral tip, where - for the case of a positive voltage applied at the sample - the tunnel current materializes into a single free electron in its emission from the gold tip and simultaneously disappears in the absorption by the gold sample. By introducing the relation (10) into (13) we obtain the result

\[ \rho_{\text{charge}}(\rho) = \frac{Ne}{\rho^3} = \frac{V}{d\rho^3 \sqrt{2e}} \quad (16) \]

On the other hand, with (6), (8) and (12) we obtain for the electric dipolar energy density \( \rho_{\text{el}} \)

\[ \rho_{\text{el}}(\rho) = \frac{N^2 e^2 d^2}{2\rho^3} \quad (17) \]

By setting \( \rho = \frac{d}{2} \) for the location of the tunnel gap we obtain for the electric dipolar surface energy \( P_{\text{el}} \)

\[ \Rightarrow P_{\text{el}} \left( \frac{d}{2} \right) = \frac{4N^2 e^2}{d} \quad (18) \]

With (10) we obtain the result

\[ P_{\text{el}} = \frac{4N^3 e^2 \sqrt{e}}{V\sqrt{2}} \quad (19) \]

In the same way, as the stationary motion of electron charge through the tunnel gap can be regarded as a rotation of an electric dipole, the motion of electronic mass \( m_{\text{el}} \) can be described as a spin of surface mass (11)

\[ s_{\text{mel}} = \frac{N}{2} m_{\text{el}} \omega \quad (20) \]
This spin of the surface mass corresponds to the spin of an electronic mass, the spin angular momentum of a single electron

\[ s_{\text{el}} = s_{\text{electron}} \quad (21) \]

To this spin we associate a kinetic energy

\[ E_{\text{kin:tunnel}} = \frac{N}{4} m_{\text{el}} \omega^2 \quad (22) \]

the motion of electronic mass \( m_{\text{el}} \) can alternatively be described as an angular momentum \( \mathcal{L} \) of electronic mass which is defined by an inertial moment \( \theta_{\text{tunnel}} \) and an angular frequency \( \omega = 2\pi f \).

\[ \mathcal{L}_{\text{tunnel}} = \theta_{\text{tunnel}} \omega \quad (23) \]

To the angular momentum we can associate a stationary spin current \( \mathbf{I}_L \) which corresponds to a kinetic energy content \( E_{\text{kin}} \) of the stationary angular momentum:

\[ I_L = \dot{\mathcal{L}}_{\text{tunnel}} = I_{\text{tunnel}} \cdot \frac{\mathcal{L}}{e} = \frac{N}{[S]} \mathcal{L} = f_e \mathcal{L} = E_{\text{kin}} = \frac{1}{2} \theta_{\text{tunnel}} \omega^2 \quad (24) \]

The kinetic energy content of the orbital angular momentum \( \ell = \frac{1}{N} \mathcal{L} \) of single tunneling electrons corresponds to a current of electronic spin \( \dot{s}_{\text{electron}} \) - the time derivative of the spin - which must be equal to the kinetic energy content \( E_{\text{kin}} \) of the tunnel current divided by the number \( N \) of electrons participating in the tunnel current:

\[ \dot{s}_{\text{electron}} = \frac{1}{2} s_{\text{electron}} \omega = \frac{E_{\text{kin}}}{N} = \frac{1}{2N} \theta_{\text{tunnel}} \omega = \frac{1}{2} \ell \quad (25) \]

For the kinetic energy content of a single tunneling electron \( E_{\text{kin:electron}} \) we obtain:

\[ E_{\text{kin:electron}} = \frac{1}{2} \theta_{\text{m_el}} \omega^2 = \frac{1}{2} \frac{1}{2N} \theta_{\text{tunnel}} \omega^2 = \frac{1}{4N} \mathcal{L} \omega = \frac{1}{4} \ell \omega \quad (26) \]
Assuming a quantized angular momentum of a single tunneling electron $\frac{h}{2\pi}$ we obtain the result

$$s_{\text{electron}} = \frac{h}{4\pi} \quad (27)$$

This result shows that our classical model of the tunneling electron is consistent with relativistic quantum theory of the electron [10].

In addition to the kinetic energy there is also a magnetic dipolar component of the energy of the tunnel current which can be expressed in terms of the transverse magnetic field $H$ which is generated by the tunnel current

$$H = -\frac{I}{\rho} n_\varphi \quad (28).$$

A dipolar magnetic energy density is attributed to the conductive shell of the tetrahedral tip

$$q_{\text{mag}}(\rho) = \frac{1}{\epsilon_0 c^2} H^2 = \frac{I^2}{\epsilon_0 c^2 \rho^2} \quad (29)$$

This leads to an integrated cross sectional magnetic dipolar energy $P_{\text{mag}}$

$$P_{\text{mag}} = \frac{e^2}{\epsilon_0 c^2} I^2 = \frac{e^2 N^2}{\epsilon_0 c^2} \quad (30)$$

Within the scope of our model, the total stationary energy content of the tunnel current through the tunnel gap is given by the magnetic dipolar energy. It must be equal to the kinetic energy of the tunnel current (22) the kinetic surface energy or surface tension of the metal shell of the tetrahedral tip,

$$\frac{N}{4} m_{\text{el}} \omega^2 = \frac{e^2 N^2}{\epsilon_0 c^2} \quad (31)$$
For the kinetic energy of a single tunneling electron we obtain the relation

$$\frac{1}{4} m_{el} \omega^2 = \frac{e^2 N}{\epsilon_o c^2} \quad (32)$$

$$\Rightarrow \omega^2 = \frac{4e^2 N}{\epsilon_o c^2 m_{el}} \quad; \quad \omega = \frac{2e \mu_0 \sqrt{N}}{\sqrt{m_{el}}} \quad (33)$$

From this kinetic surface energy, we derive an inertial transverse torque of a single electron of the tunneling current $w_{tunnel}$

$$w_{tunnel} = \frac{E_{kin,electron}}{2\pi} = \frac{m_{el}}{8\pi} \omega^2 = \frac{e^2 N}{2\pi \epsilon_o c^2} = \frac{e \sqrt{N} \sqrt{m_{el} \omega}}{c4\pi \sqrt{\epsilon_o}} \quad (34)$$

Inserting Sommerfeld’s dimensionless fine structure constant $\alpha = \frac{e^2}{2\epsilon_0 \hbar c}$ into the equation (33) we obtain the result:

$$\frac{e^2 N}{2\pi \epsilon_o c^2} = \frac{e \sqrt{N} \sqrt{m_{el} \omega}}{c4\pi \sqrt{\epsilon_o}} = \frac{\hbar \alpha N}{2\pi c} \quad (35)$$

From (34) we can also derive an expression for the angular frequency

$$\Rightarrow \omega = \frac{2e \sqrt{N}}{c \sqrt{\epsilon_0 m_{el}}} \quad (36)$$

The transverse torque of an electron must be the same as the inertial torque of a single electronic mass. As the tunnel current propagates in the longitudinal $z$-direction, this transverse inertial torque corresponds to an inertial torque $w_{electron}$ of an electron at rest.

$$w_{tunnel} = w_{electron} = \frac{1}{2} \dot{s}_{mel} \quad (37)$$
The inertial torque of an electron at rest is due to its intrinsic kinetic energy $hf$ which is related to the intrinsic quantized spin of the rest mass of a single electron (27)

$$s_{\text{electron}} = \frac{h}{4\pi}$$ (38)

From these results we infer that the transverse inertial torque of the tunnel current corresponds to an intrinsic distributed torque density of the electron which is not localized in the tunnel gap and can therefore acts on the environment of the tunnel gap in a similar way as the dipolar stationary surface charge and the magnetic field density of a single electron tunneling current. Due to the well-known equivalence principle underlying Einstein’s general theory of relativity, this inertial torque cannot be distinguished from a gravitational torque of a single electron and therefore, the action of a stationary tunnel current on an electrically neutral environment can be regarded as being due to the action of gravitational forces and cannot be distinguished from magnetic forces. This interpretation is in complete accord with Bernhard Riemann’s draft of a general theory of the physical space [8] which contains a complete unified theory of electromagnetism and gravitation and can be regarded as a modified general theory of relativity with respect to Albert Einstein’s theory. The action of the inertial torque of the tunneling electron on an electrically neutral environment can be described by a homogeneously distributed density of an azimuthal torsional spring constant $k_{\text{electron}}$ of the electron:

$$k_{\text{electron}} = \frac{dw_{\text{electron}}}{d\varphi} = \frac{dw_{\text{electron}}}{d\omega} \cdot \frac{d\omega}{d\varphi} = \frac{1}{2\pi} \frac{dw_{\text{electron}}}{d\omega}$$ (39)

with (34)we obtain the result

$$\frac{dw_{\text{tunnel}}}{d\varphi} = \frac{e\sqrt{N}\sqrt{m_{e\text{l}}}}{c8\pi^2\sqrt{\varepsilon_0}}$$ (40)
Influence of a stationary tunnel current on the Raman spectra.

The transverse differential torque of the tunnel current induces a maximum energy gain on a normally incident photon due to the transfer of angular momentum from electrons to photons, as the polarization axis of the photons rotates by a polar angle $\Delta \theta = \frac{\pi}{2}$ in a single reflection step of the retroreflection. Energy is transferred from the tunnel current to the reflected photon only in the second reflection step when the rotation is driven by the torsional force of the tunnel current as indicated in fig.1

$$h\Delta_+ f = \frac{\pi}{2} \frac{d\omega_{\text{tunnel}}}{d\theta} = \frac{1}{16\pi} \frac{e\sqrt{N m_{\text{el}}}}{c\sqrt{\varepsilon_0}} \cdot s^{-2} \quad (41)$$

The current induced blueshift $h\Delta_+ f$ depends on the wavelength of the incident light but only on the square root of the frequency $N$ of electron passage through the tunnelgap. With (2) we obtain for the total frequency shift

$$h\Delta f = h\Delta_+ f - h\Delta_- f = \frac{1}{4\pi} \left( e^4 \sqrt{\mu_0 N m_{\text{el}}} - h\Delta_+ f \right)$$

$$\Rightarrow \frac{\Delta f}{f} = \frac{1}{4\pi} \left( e^4 \sqrt{\mu_0 N m_{\text{el}}} - 1 \right) = \lambda \Delta \frac{1}{\lambda}$$

$$\Rightarrow \Delta \left( \frac{1}{\lambda} \right) = \Delta_+ \left( \frac{1}{\lambda} \right) - \Delta_- \left( \frac{1}{\lambda} \right) = \left( \frac{e}{16\pi \sqrt{\mu_0 N m_{\text{el}}}} - \frac{1}{4\pi \lambda} \right)$$

$$\Rightarrow \Delta \frac{1}{\lambda} = \left( \frac{e}{4\pi} \sqrt{\mu_0 m_{\text{el}} \cdot \sqrt{N} s^{-1}} - 1 \right) \cdot 1257 \text{ cm}^{-1} \quad (42)$$

With
\[ e = 1,602 \cdot 10^{-19} \text{ As}; \ m_{el} = 9,1 \cdot 10^{-31} \text{ kg}; \ h = 6,62 \cdot 10^{-34} \text{ m}^2 \text{ kg s}^{-1}; \ \mu_0 = 1,2566 \cdot 10^{-6} \text{ H m}^{-1} \text{ or alternatively } \mu_0 = 1,2566 \cdot 10^{-6} \text{ N A}^{-2} \]

\[ \Rightarrow \frac{e}{4h} \sqrt{\mu_0 m_{el}} = 6,47 \cdot 10^{-5} \]

Calculated values for the spectral shifts are summarized in Table 1. In Fig 2 the calculated values are indicated by the coloured bars. A fair coincidence between experimental data and the calculation is obtained. This Interpretation of the spectra recovers the general property of Raman spectroscopy, that the Raman shift of the scattered light of a solid ponderable body is scale invariant with respect to the wavelength or photon energy of the incident beam of monochromatic electromagnetic radiation which distinguishes Raman scattering from other inelastic scattering processes like molecular fluorescence or solid state luminescence or particle plasmon scattering, where a resonant scattering process has a wavelength which is determined by the resonances of a geometrically confined structure of ponderable matter.

<table>
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<th>( I_{\text{tunnel/A}} )</th>
<th>( \sqrt{N} )</th>
<th>( \frac{e}{4h} \sqrt{\mu_0 m_{el}} \cdot 1257 \text{ cm}^{-1} )</th>
<th>( \Delta_+ \left( \frac{1}{\lambda} \right) \text{ cm}^{-1} )</th>
<th>( \Delta_- \left( \frac{1}{\lambda} \right) \text{ cm}^{-1} )</th>
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</table>
Conclusions

We arrived at a determination of the position of the maximum in the broad background of the Raman spectra which coincides with the experimental results within experimental uncertainties in the order of 100 cm\(^{-1}\). It is remarkable, that only the known values of the current and the wavelength and fundamental constants enter into the calculation. No adjustable parameters are needed. Our classical explanation of the torque of the tunneling electrons is consistent with the spin \(\frac{h}{4\pi}\) of an electron as known from relativistic quantum theory. We did not yet deal with the determination of the width of the broad band background. We intend to determine the width by introducing an angular distribution of the angle of incidence of the photon, which, within our model of the photon is considered as a hemispherical wavefront of a numerical aperture 1 [8,9]. Therefore, we have to consider the whole angular spectrum of the spherical wave to determine the redshift which depends on the angle of incidence. In order to elucidate the origin of other features of the spectra, more systematic experiments have to be performed. The narrow line spectra are tentatively attributed to the adsorbed molecular layer of bipyridine and possibly other adsorbed molecular layers. Other less pronounced assymetric and symetric deviations from the the smooth wide band electronic background may be related to Fano resonances between the narrow line molecular resonances and the electronic continuum or to coupled oscillations of molecular aggregates respectively. We have to assume, that at ambient conditions a water layer and other components of the atmosphere are adsorbed to the metal film which may give rise to coupled molecular oscillations. Last
not least, the local granular roughness of the metal film and corrugations or deviations from the assumed perfect shape of the rectangular apex of the tetrahedral tip as well as chemical inhomogeneities of the glass substrate are expected to have an effect on the spectrum. It is well known, that the radius of curvature of a metal tip has a strong effect on the TERS spectra [3] and the metal particle properties determine the SES spectra [4]

Discussion

In a more technically oriented description, the tunnel gap can be regarded as an optoelectronic device which can be characterized by the I/V characteristics as a function of the intensity of the incident light. The I/V Characteristics are encoded in the complex admittance $A_{tunnel} e^{i\phi_{tunnel}} = \frac{I}{V}$ of the device. In this expression $I$ and $V$ are complex valued observables but the imaginary part of $V$ is zero. According to our interpretation the current induced blueshift of the Raman spectrum due to the current is described by the formula (41)

$$\Delta_+ \left( \frac{1}{\lambda} \right) = \frac{e}{16\hbar \pi} \sqrt{\mu_0 N m_{el}} \cdot \left( \frac{1}{\lambda} \right)$$

and the energy gain $\hbar \Delta_+ f$ of the photon is due to the effect of the torque of the tunnel current $w_{tunnel}$ on the incident photons

$$\hbar \Delta_+ f = \frac{1}{8} w_{tunnel} = \frac{e}{16c\pi} \sqrt{N m_{el}} \sqrt{\epsilon_0}$$

which can be expressed in different ways as a function of the stationary content of kinetic energy, dipolar electric or dipolar magnetic Energy of the tunnel gap respectively.
\[ w_{\text{tunnel}} = \frac{1}{2\pi} E_{\text{kin}} = \frac{e\sqrt{Nm_e}}{2\pi c\sqrt{\varepsilon_0}} = \frac{1}{4\pi} \cdot eV_{\text{tunnel}}^2 = \frac{1}{4\pi} \cdot \mu_0I_{\text{tunnel}}^2 \]

The equation:

\[ eV_{\text{tunnel}}^2 = \mu_0I_{\text{tunnel}}^2 \]

can be used to derive the complex Admittance of the tunnel gap:

\[ A_{\text{tunnel}} e^{i\phi_{\text{tunnel}}} = \frac{I_{\text{tunnel}}}{V_{\text{tunnel}}} \]

From this result we derive in the following passage the conclusion, that the Raman spectrum can be regarded as the admittance spectrum of the tunnel gap. Since the tunnel current is a non linear function of the tunnel voltage, the tunnel gap has a non linear admittance as is well known. The admittance is thus a non linear function of the tunnel current or the number \( N \), the frequency of electron passage through the tunnel gap, and the shape of the I/V characteristic can be characterized by the derivative of the complex admittance as function of the tunnel current or the tunnel frequency \( N \). Regarding the influence of the light on the admittance one can say that the light intensity has no influence on the complex admittance, as only the wavelength of light enters into the expression of the energy gain of the stationary energy density of the tunnel gap as a function of the incident light. On the other hand the intensity of the scattered light increases once the number flux of incident photons exceeds the stationary number flux of electrons through the tunnel gap. In this situation, the stationary energy gain of the tunnel gap is replaced by an increase in the intensity of the inelastically scattered light which can be regarded as a process of emission of light which is stimulated by the current. This realm is not entered in the
experiments and will not be discussed further here. In order to derive the complex admittance as a function of the tunnel current we set:

\[ A_{\text{tunnel}}^2 e^{2i\varphi_{\text{tunnel}}} = \frac{I_{\text{tunnel}}^2}{V_{\text{tunnel}}^2} e^{2i\varphi_{\text{tunnel}}} = \frac{e}{\mu_0} = \frac{N^2 e^3}{\mu_0 |S|^2}; \quad I_{\text{tunnel}} = A_{\text{tunnel}} e^{i\varphi_{\text{tunnel}}} = \sqrt{\frac{e}{\mu_0}} \]

Since \( \sqrt{\frac{e}{\mu_0}} \) is a real number

\[ \Rightarrow A_{\text{tunnel}} = \sqrt{\frac{e}{\mu_0}} \Rightarrow \frac{e}{\mu_0} e^{2i\varphi_{\text{tunnel}}} - \frac{e}{\mu_0} = 0 \]

\[ \Rightarrow e^{2i\varphi_{\text{tunnel}}} - 1 = 0 \]

\[ \Rightarrow \varphi_{\text{tunnel}} = -\frac{\pi}{2} \Rightarrow A_{\text{tunnel}}^2 = \frac{I_{\text{tunnel}}^2}{V_{\text{tunnel}}^2} \left( e^{-i\frac{\pi}{2}} \right)^2 = \frac{I_{\text{tunnel}}^2}{V_{\text{tunnel}}^2} \]

\[ \frac{\partial A_{\text{tunnel}}}{\partial I_{\text{tunnel}}} = \frac{2I_{\text{tunnel}}}{V_{\text{tunnel}}^2} \]

We conclude, that the tunnel gap has a positive admittance. Therefore it can be regarded as a dipolar tunnel transistor device which is affected by photons. The Raman spectrum can be regarded as a linear color image of the admittance spectrum of the tunnel gap or a mirror image of the impedance spectrum. As the Raman spectrum is a phonon spectrum it can be regarded as an acoustic spectrum, whereas the Impedance spectrum corresponds to its dielectric or electromagnetic spectrum. We noticed, that the Raman spectrum of the single electron tunnel gap leads to a derivation of the distance of the tunnel gap, if the externally applied tunnel voltage is known. Since molecules contain chemical bonds, which can be regarded as ideally conducting tunnel bridges, where no external voltage is applied and the local voltage is determined by the charge distribution within the molecule, our
interpretation illustrates the close relation between spectral information in Raman spectroscopy and the molecular spatial structure of molecules. The network of chemical bonds within a molecule can be regarded as a network of circular currents of electronic and nuclear charge, where local surface charges arise at spatial inhomogeneities of the internal charge density distribution within the molecular structure. The common interpretation of the Raman shift of molecular structures as being associated to the stationary excitation of acoustic or rotational molecular vibrations is here replaced by the interpretation of the Raman shift as being due to a displacement of the center of gravity of the molecular moiety which is associated to a stationary acoustic vibration being excited by the irradiation with light. The temporal information on the frequency of the molecular oscillation is thus replaced by a spatial information on the charge density gradient within the molecular moiety. In the configuration of a tunnel gap as a single atomic gold tip and a planar thin film of gold, the stationary tunneling of electrons through a tunnel gap cannot be distinguished from a stationary tunneling of a gold atom, which is dressed with a single electron shell, through the tunnel gap in a similar way as hydrogen tunneling in hydrogen bridges can be regarded as a tunneling of a proton which is dressed with an electron, a dipolar ion tunneling process. From the point of view of thermodynamics, the influence of photons on a tunnel current can be regarded as photon driven energy pumping process where energy is delivered from the tunnel current to the electromagnetic field. The influence of photons on the tunnel current can be regarded as a current induced gain of energy of the photonic electromagnetic field. The tunnel current pumps energy into the electromagnetic field of the photons. At the origin of this energy pump mechanism is a transformation of Electron orbital angular momentum to an increased spin density of the tunnel gap. The stationary single
electron tunnel current carries an isotropic azimuthal orbital angular momentum density which corresponds to the spin $\frac{h}{4\pi}$ of the electron. The spin flux corresponds to an inertial torque which acts on the photons of spin $\frac{h}{2\pi}$ of the incident beam and leads to an increase in energy of the scattered photons. This corresponds to a gain of energy and momentum of the electromagnetic field. The conical conductive shell can be considered as a Quantum driven Spin Orbit Transformer (SPOT) which can also be considered as a quantum energy converter.

**Outlook**

In this context it will be interesting to apply the concept of the SPOT to designs of supramolecular constructs for artificial photosynthesis. A bimolecular tunnel gap or a chemical bond between a bimolecular structure was already shown to be essential for an explanation of the generation of electron- and proton- motive forces by photo-electrochemical processes in natural photosynthesis [13,14] and led to suggestions for supramolecular constructs for the primary electron tunneling processes of charge separation in artificial photosynthetic systems [13].

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