Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Explanation of the Size Dependent In-Plane Optical Resonance of Triangular Silver Nanoprisms

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Supporting Information

General description of the proposed model

It is a known phenomenon in the science, that an issue can be explained by different approaches or models. Within this work we discuss an empirically found model, which is based on simplest quantum mechanics to describe the size dependence of the optical in-plane resonance of triangular shaped silver nanoprisms. In contrast to classic electrodynamics, no collective coherent oscillators are modeled, which oscillate with the frequency of the incident light and are subjected to various damping mechanisms (compare to Fig. S1a). Here, the occurring resonance is not described by the excitation of a plasmon but by the excitation of an electron (Fig. S1b). The basis of the model is a one-photon-one-electron process. This description is analogous to a molecular electronic excitation. The assumption is that nanoparticles are materials with blurred band gaps (compare to Fig. 2). The state density distributions of the occupied states and the unoccupied states can be approximated by Gaussian functions, which might overlap depending on the particle size. The smaller the nanoparticle is the higher is the energetic distance of the

functions of the state density distributions. The optical resonance spectra can be obtained by multiplying the state density of each energy value of the occupied state with the state density distribution of each energy value of the unoccupied state.

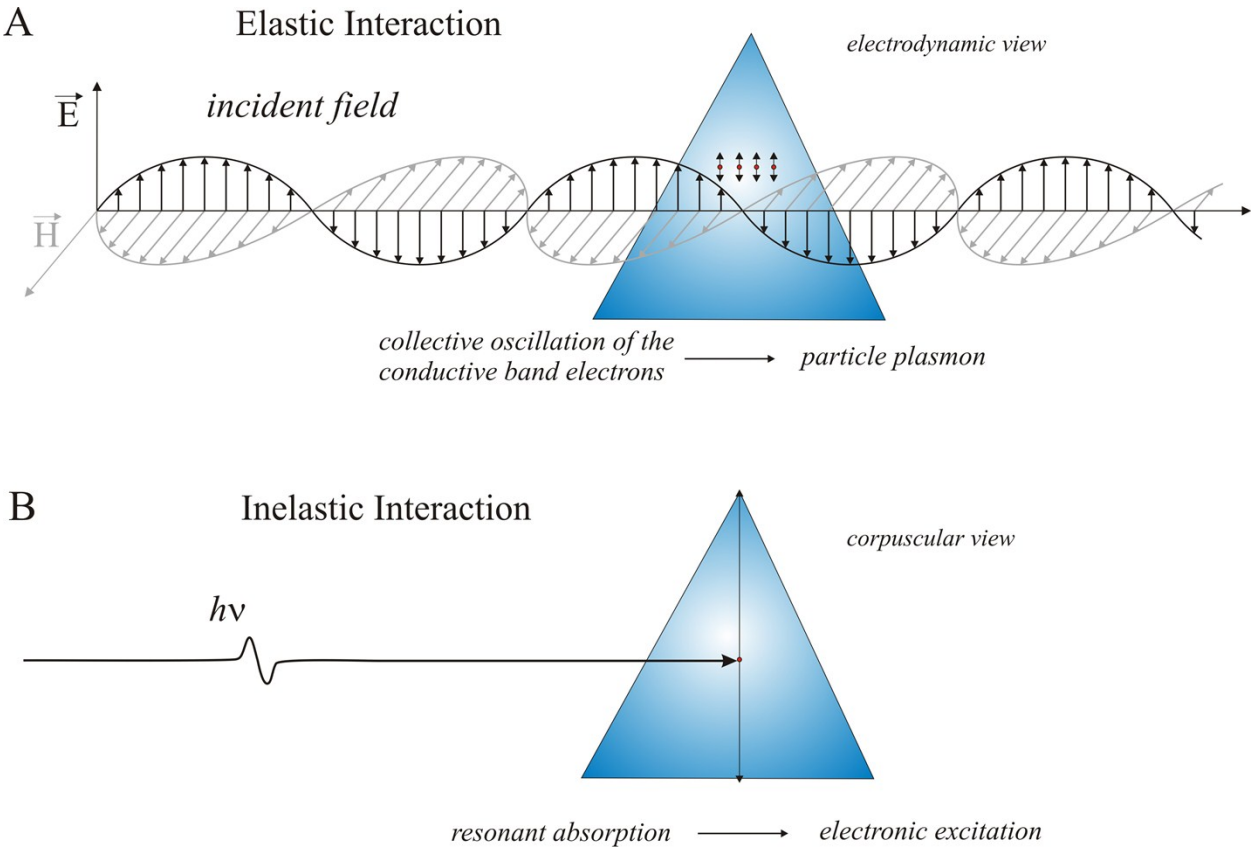

Fig. S1: Comparison of two different views on the origin of resonance peaks in optical spectroscopy. A) Illustration of the classic electrodynamic approach. The localized surface plasmon is a quasi-particle that is assigned to the collective coherent oscillation of all conductive band electrons. B) Scheme of an inelastic interaction, where the description is based on the resonance conditions of one single electron. Here, the resonance is explained by the excitation of a single electron by one photon.

Correlation of DCS and SEM measurements

Althought differential centrifugal sedimentation spectra are very useful regarding information about the sample homogeneity, no information about geometry parameters can be derived from these measurements in case of shape anisotropic nanoparticles. Thus, SEM analyses were carried out for different prism samples to determine the edge length. The diagram in **Fig. S3** shows the correlation between the DCS determined Stokes equivalent sedimentation diameter and the SEM determined edge length of the silver nanoprisms. An overview of the values of the fit line is given in Table S1, which are helpful for a quick assessment of the prisms edge length after determination of the sedimentation diameter and which are in good agreement with equation (1) $\lambda_{max} = 2\,(b_0 + b)$ that enables an estimation of the prisms edge length after UV-Vis analyses.

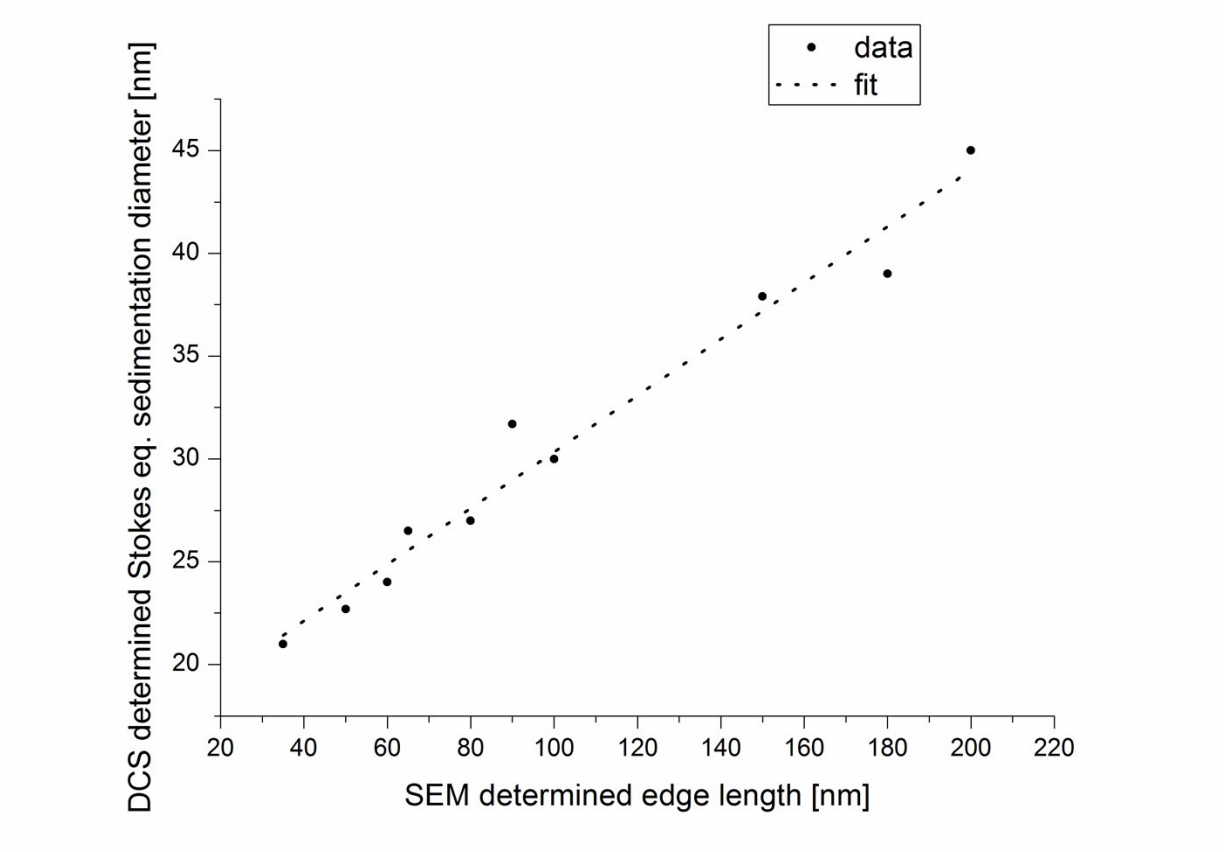

Fig. S3: Interrelation of DCS and SEM data.

Table S1: Values of the fit line shown in **Fig. S2**:

DCS determined d [nm]	corresponding edge length [nm]
21.7	36.7
21.9	38.3
22.1	40.0
22.3	41.7
22.6	43.3
22.8	45.0
23.0	46.7
23.3	48.3
23.5	50.0
23.7	51.7
23.9	53.3
24.2	55.0
24.4	56.7
24.6	58.3
24.9	60.0
25.1	61.7
25.3	63.3
25.5	65.0
25.8	66.7
26.0	68.3
26.3	70.0
26.5	71.7
26.7	73.3
26.9	75.0
27.2	76.7
27.4	78.3
27.6	80.0
27.9	81.7
28.0	83.3
28.3	85.0
28.6	86.7
28.8	88.3
29.0	90.0

29.2	91.7
29.5	93.3
29.7	95.0
29.9	96.7
30.2	98.3
30.4	100.0
30.6	101.7
30.8	103.3
31.0	105.0
31.3	106.7
31.5	108.3
31.8	110.0
31.9	111.7
32.2	113.3
32.4	115.0
32.7	116.7
32.9	118.3
33.1	120.0
33.3	121.7
33.6	123.3
33.8	125.0
34.0	126.7
34.3	128.3
34.5	130.0
34.7	131.7
34.9	133.3
35.2	135.0
35.4	136.7
35.6	138.3
35.9	140.0
36.0	141.7
36.3	143.3
36.5	145.0
36.8	146.7
37.0	148.3
37.2	150.0
37.5	151.7
37.7	153.3
37.9	155.0
38.1	156.7
38.4	158.3
38.6	160.0
38.8	161.7

39.1	163.3
39.3	165.0
39.5	166.7
39.7	168.3
39.9	170.0
40.2	171.7
40.4	173.3
40.7	175.0
40.9	176.7
41.1	178.3
41.3	180.0
41.6	181.7
41.8	183.3
42.0	185.0
42.3	186.7
42.5	188.3
42.7	190.0
42.9	191.7
43.2	193.3
43.4	195.0
43.6	196.7
43.8	198.3
44.0	200.0