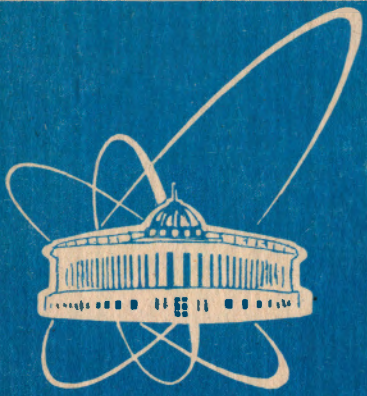

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MULTIPOLE OPTICAL RESPONSE OF SPHERICAL SODIUM CLUSTERS: COUPLING OF SURFACE AND VOLUME MODES

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Мультипольный оптический отклик сферических натриевых кластеров: связь поверхностных и объемных степеней свободы

В схематическом приближении хаотических фаз (СПХФ) учтена связь коллективных $E\lambda$ осцилляций поверхностного и объемного типа, что значительно улучшило описание дипольного плазмона в нейтральных и заряженных ($Z=+1$) натриевых кластерах. Хорошее согласие полученных результатов с экспериментальными данными свидетельствует о том, что сепарабельное приближение, использованное для остаточного взаимодействия в СПХФ, вполне правомерно. Сделаны предсказания для E2 и E3 коллективных возбуждений. Вычисления выполнены с одночастичными схемами Кона-Шема и Вудса-Саксона. Для потенциала Вудса-Саксона предложены новые параметры.

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Multipole Optical Response of Spherical Sodium Clusters: Coupling of Surface and Volume Modes

The coupling of surface and volume collective $E\lambda$ oscillations is taken into account in the schematic random-phase approximation (SRPA). This leads to a considerable improvement of description of the dipole plasmon in neutral and singly charged ($Z=+1$) sodium clusters. Good agreement of the SRPA results with experimental data testifies to the applicability of the separable approximation used in the SRPA residual forces. The predictions for E2 and E3 collective excitations are presented. The calculations were performed with the Kohn-Sham and Woods-Saxon single-particle schemes. New parameters for the Woods-Saxon potential are proposed.

The investigation has been performed at the Bogoliubov Laboratory of Theoretical Physics, JINR.

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1. Introduction

Collective oscillations in metal clusters (MC), first of all the dipole plasmon, is now a field of intensive investigations (see, reviews [1-5]). The RPA methods describing the Landau damping are especially useful in this field [1-4,6-11]. Fragmentation of the collective strength over particle-hole excitations (Landau damping) plays an important role in many MC characteristics, particularly in forming the dipole plasmon width.

The SRPA method (otherwise called as the vibrating potential model) has recently been proposed for MC [9-11]. This method exploits the separable approximation when the residual two-body forces are presented in the factorized form through the sigle-particle (particle-hole) matrix elements: $V(p_1,p_2,h_2,h_1) = \kappa q(p_1,h_1)q(p_2,h_2)$ (in the time-dependent formalism [11], the factorization of the density variation into time-dependent and spatial parts is used). The separable approximation allows to reduce the RPA matrix to the simple equation, that drastically simplifies the calculations. This is important in the cases of deformed or very large MC when an impressive particle-hole configuration space is used. The SRPA calculations with the Woods-Saxon single-particle scheme and surface self-consistent residual interaction have been performed for a dipole plasmon in spherical and deformed MC in [11] and good perspectives of the method have been demonstrated. However, like many other RPA methods without explicit treating the ionic subsystem [4], the calculations [11] somewhat overestimated plasmon energies, especially for small clusters. Also, for clusters with $N_e > 20$ (N_e is the number of valence electrons) too strong high-energy strength was predicted. For example, for Na_{26} and Na_{40}, the dipole strength at the energies $E > 3.4$ eV exhausted 30% and 44%, respectively, while the corresponding experimental data [12,13] gave 10-15% for clusters of this size and up to 20-30% for larger clusters [23]. Such a general blueshift of the dipole strength led to a considerable underestimation of the static dipole polarizabilities.

In the present paper, we remove these shortcomings by using the Kohn-Sham single-particle scheme with a diffused jellium and taking into account

the coupling of surface and volume modes. The diffuseness of the jellium simulates a pseudopotential folding [20] and, as is shown below, leads to the redshift of the plasmon energy attaching it to the experimental value. The coupling of surface and volume modes is included to decrease the high-energy strength [1,4]. The volume modes are introduced following the local RPA prescription [14]. As is shown below, such a coupling considerably improves the description of the dipole plasmon. This finally provides strong grounds in favour of the applicability of the separable approximation. The calculations have been performed with the diffused Kohn-Sham [15,16] and Wood-Saxon single-particle schemes. The latter was done to demonstrate the applicability of the Woods-Saxon potential in the RPA description of collective oscillations in neutral and singly charged MC.

2. Main SRPA equations

We start with the Kohn-Sham energy functional for a system of N_e valence electrons

$$E\{n(\vec{r},t),\tau(\vec{r})\} = 1/2\int \tau(\vec{r},t)d\vec{r} + \int v(n(\vec{r},t))d\vec{r}$$
$$+ 1/2\int\int \frac{(n(\vec{r},t)-n_i(\vec{r}))(n(\vec{r}_1,t)-n_i(\vec{r}_1))}{|\vec{r}-\vec{r}_1|}d\vec{r}d\vec{r}_1, \qquad (1)$$

which includes kinetic energy, exchange-correlation (in local density approximation [17]) and Coulomb terms, respectively. Here, $n(\vec{r},t) = \Sigma_k|\phi_k(\vec{r},t)|^2$ and $\tau(\vec{r},t) = \Sigma_k|\nabla\phi_k(\vec{r},t)|^2$ are density and kinetic energy density of valence electrons, $n_i(\vec{r})$ is the ionic density in the jellium approximation and $\phi_k(\vec{r},t)$ is a single-particle wave function. The convention $e = m_e = \hbar = 1$ is used.

The time-dependent single-particle potential is obtained as

$$H(\vec{r},t)\phi_k(\vec{r},t) = \frac{\delta E}{\delta\phi_k^*(\vec{r},t)} \qquad (2)$$

and in the small-amplitude limit of collective motion is written as a sum of the static

$$H_0(\vec{r}) = -\frac{\nabla^2}{2} + (\frac{dv}{dn})_{n=n_0} + \int \frac{n_0(\vec{r}_1)-n_i(\vec{r}_1)}{|\vec{r}-\vec{r}_1|}d\vec{r}_1 \qquad (3)$$

and dynamical parts

$$\delta H(\vec{r},t) = (\frac{d^2v}{dn^2})_{n=n_0}\delta n(\vec{r},t) + \int \frac{\delta n(\vec{r}_1,t)}{|\vec{r}-\vec{r}_1|}d\vec{r}_1 \qquad (4)$$

where $n(\vec{r},t) = n_0(\vec{r}) + \delta n(\vec{r},t)$ and $n_0(\vec{r})$ is the static ground state density. Exp. (3) constitutes the Kohn-Sham single-particle potential.

The perturbed time-dependent wave function of the system is defined through the scaling transformation

$$|\Psi(t)>= e^{i\alpha_{\lambda\mu 1}(t)[H_0,f_{\lambda\mu 1}]}...e^{i\alpha_{\lambda\mu K}(t)[H_0,f_{\lambda\mu K}]}|0> . \qquad (5)$$

Here, $|0>$ is the ground-state wave function ($H_0|0>=0$), both $|0>$ and $|\Psi(t)>$ are the Slater determinants, $\alpha_{\lambda\mu k}(t) = \alpha^{(0)}_{\lambda\mu k}cos(\omega t)$ are harmonic collective variables, $f_{\lambda\mu k}(\vec{r}) = r^{p_k}(Y_{\lambda\mu}(\theta,\phi) + Y^{\dagger}_{\lambda\mu}(\theta,\phi))$ $(k = 1,...,K)$ are local hermitian coordinate operators.

Having used (5), the density variation is written as

$$\delta n(\vec{r},t) = \sum_{k=1}^{K} \alpha_{\lambda\mu k}(t)(\nabla n_0(\vec{r})\cdot\nabla f_{\lambda\mu k}(\vec{r}) + n_0(\vec{r})\Delta f_{\lambda\mu k}(\vec{r})) \qquad (6)$$

and includes both the surface $\sim \nabla n_0(\vec{r})$ and volume $\sim n_0(\vec{r})$ terms. For divergency-free operator with $p = \lambda$, exp. (6) has only the term of the surface character. Just this case was considered in [11]. The operators with $p_k > \lambda$ lead to a volume collective motion. The importance of volume degrees of freedom for dipole excitations was justified for both atomic nuclei [18] and MC [1,14,19]. In [14], the set of local operators with $p = 1,4,7,10,13$ was proposed. Our study has shown that the sets $p = 1,4,7,10$, $p = 2,4,6,8$ and $p = 3,5,7,9$ are most appropriate for the description of dipole, quadrupole and octupole oscillations, respectively. Just these sets have been used in the present calculations when the coupling of surface and volume modes was taken into account.

Substituting (6) into (4) we have

$$\delta H(\vec{r},t) = \sum_{k=1}^{K} \alpha_{\lambda\mu k}(t) Q_{\lambda\mu k}(\vec{r}) \qquad (7)$$

with

$$Q_{\lambda\mu k}(\vec{r}) = (\frac{d^2v}{dn^2})_{n=n_0}(\nabla n_0(\vec{r})\cdot\nabla f_{\lambda\mu k}(\vec{r}) + n_0(\vec{r})\Delta f_{\lambda\mu k}(\vec{r}))$$

$$+ \int \frac{(\nabla n_0(\vec{r}_1)\cdot\nabla f_{\lambda\mu k}(\vec{r}_1) + n_0(\vec{r}_1)\Delta f_{\lambda\mu k}(\vec{r}_1))}{|\vec{r}-\vec{r}_1|}d\vec{r}_1. \qquad (8)$$

Finally, substituting the Hamiltonian $H(\vec{r},t) = H_0(\vec{r}) + \delta H(\vec{r},t)$ into the time dependent Schrödinger equation and using the linear response of the operator $Q_{\lambda\mu k}(\vec{r})$

$$\delta Q_{\lambda\mu k}(t) = \int Q_{\lambda\mu k}(\vec{r})\delta n(\vec{r},t)d\vec{r} = -\sum_{k'=1}^{K} \alpha_{\lambda\mu k'}(t)\kappa^{-1}_{\lambda\mu kk'} \qquad (9)$$

with

$$\kappa^{-1}_{\lambda\mu kk'} = -\int Q_{\lambda\mu k}(\vec{r})(\nabla n_0(\vec{r})\cdot\nabla f_{\lambda\mu k'}(\vec{r}) + n_0(\vec{r})\Delta f_{\lambda\mu k'}(\vec{r}))d\vec{r} \qquad (10)$$

one gets the system of homogeneous equations to determine amplitudes $\alpha^{(0)}_{\lambda\mu k}$:

$$\sum_{k'=1}^{K} S_{\lambda\mu kk'}(\omega)\alpha^{(0)}_{\lambda\mu k'} = 0 \qquad (11)$$

with

$$S_{\lambda\mu kk'}(\omega) = \sum_{ph} \frac{<p|Q_{\lambda\mu k}|h><p|Q_{\lambda\mu k'}|h>\epsilon_{ph}}{\epsilon^2_{ph}-\omega^2} - \frac{1}{2\kappa_{\lambda\mu kk'}}. \qquad (12)$$

The amplitudes $\alpha^{(0)}_{\lambda\mu k}$ regulate the ratios between contributions of different local operators $f_{\lambda\mu k}(\vec{r})$ to the collective states. It should be emphasized that these amplitudes are not an input parameters but are calculated, i.e. the system chooses itself the most optimal contributions of the input local operators.

The condition

$$det\,|\,S_{\lambda\mu kk'}(\omega)\,|= 0 \qquad (13)$$

provides non-trivial solutions to the system (11) and represents the SRPA dispersion equation for eigenenergies ω_t. In (12), ϵ_{ph} is the energy of a particle-hole excitation and $|\,p>$ and $|\,h>$ are particle and hole eigenstates of the static Hamiltonian (3). It is seen that $\kappa_{\lambda\mu kk'}$ have a physical meaning of the strength constants of the residual forces (8). Due to the surface-volume coupling, non-diagonal strength constants take place.

3. Results and discussion

The Kohn-Sham with sharp and diffused jellium and Woods-Saxon single-particle schemes were used for calculation of the single-particle wave functions and energies. For both neutral and charged clusters, we used the same parameters of the Kohn-Sham jellium: $r_{WS} = 3.96 a.u. = 2.09 \AA$ and $a_0 = 1 a.u. = 0.529 \AA$ ($a_0 = 0$ for sharp jellium) [16].

The parameters of the Woods-Saxon potential $V_0(r) = \frac{V_0}{1+exp[(r-R)/a_0]}$ ($r_0 = 2.4 \AA$, $V_0 = -5.7$ eV and $a_0 = 1.11 \AA$ for neutral clusters and $r_0 = 2.5 \AA$, $V_0 = -7.2$ eV and $a_0 = 1.25 \AA$ for singly charged clusters) were adjusted so as to reproduce on average the diffused Kohn-Sham ground state densities. The size region with $N_e = 8 - 138$ was covered. As is seen from Fig.1, the densities are well fitted even for charged clusters whose Kohn-Sham potentials deviate considerably from the Wood-Saxon form in the surface region and beyond. Fig.3 demonstrates that the Woods-Saxon potential with the above parameters provides almost the same SRPA results as the Kohn-Sham scheme. It should be noted that the Woods-Saxon parameters, $r_0 = 2.25 \AA$, $V_0 = -6$ eV and $a_0 = 0.74 \AA$, proposed in [21] for neutral clusters lead to an overestimation of the plasmon energy and high-energy strength.

Two main kinds of the SRPA calculations are presented in Figs. 2-4: with and without coupling of surface modes with volume ones. In the first case, the sets of four local operators $f_{\lambda\mu k}(r)$ mentioned in the previous section have been used. In the second case, when volume modes are neglected, only the operators with $p_k = \lambda$ have been taken into account. The results of the calculations are presented in the form of the normalized strength function

$$\sigma(E\lambda,\omega) = \sum_i \omega_i B(E\lambda, gr \to \omega_i)\rho(\omega - \omega_i)/S(E1) \qquad (14)$$

where $\rho(\omega - \omega_i) = \frac{1}{2\pi}\frac{\Delta}{(\omega-\omega_i)^2+(\Delta/2)^2}$ is the weight function with the averaging parameter $\Delta = 0.05 eV$, $B(E\lambda, gr \to \omega_i)$ is the reduced probability of the $E\lambda$ transition from the ground state to the one-phonon state with

excitation energy ω_i and $S(E1)$ is the energy-weighted sum rule

$$S(E\lambda) = \sum_i \omega_i B(E\lambda, gr \to \omega_i) = \frac{\hbar^2 e^2}{8\pi m_e}\lambda(2\lambda+1)^2 N < r^{2\lambda-2} > . \qquad (15)$$

The expression (14) has a form similar to the photo-absorption cross section for dipole excitations.

Let us consider results of the calculations. Fig.2 demonstrates that jellium diffuseness leads to a considerable redshift of the plasmon energy and thus improves the agreement with the experimental data. If only divergency-free operator (p=1) is used, the calculations give rather strong high-energy peaks at 3.5-4.5 eV in both cases of diffused and sharp jellium. A similar result was obtained in ref. [11]. At the same time, the experiment [12,13] does supports so strong much high-energy strength. The description is improved if the coupling with volume modes is taken into account (p=1,4,7,10). Then, as is seen from Fig.2, the high-energy strength is strongly redshifted and the main dipole strength is concentrated in the region 2.5-3.5 eV.

The main SRPA results for the dipole plasmon, obtained with the coupling of surface and volume modes, are presented in Fig.3 and Table 1. It is seen that plasmon energies of charged clusters are slightly blueshifted compared to the resonance energies of neutral ones. In clusters with $N_e = 40, 58$ and 92, a considerable Landau damping takes place which should influence much the resonance widths. Table 1 shows that the calculated plasmon energies are in nice agreement with the experimental data. The correct tendency of increasing plasmon energy with a cluster size is in general reproduced. A good description of the static dipole polarizability $SDP = \sum_i \omega_i^{-1} B(E\lambda, gr \to \omega_i)$ is also achieved.

Fig.4 exhibits the SRPA results for E2 and E3 collective oscillations in singly charged clusters. It is seen that E2 and E3 strengths are mainly concentrated in the energy regions 2.5-3.5 and 3-4 eV, respectively. Main peaks are well pronounced. It is interesting that, like the dipole case, the coupling with volume modes noticeably influences E2 and E3 excitations: the high-energy strength is redshifted and the resonances become more concentrated.

Table 1: Energy centroids of the dipole plasmon $\bar{\omega}$ (in eV) and SDP (in units R^3 with $R = r_{WS}N^{1/3}$, $r_{WS} = 3.96$ a.u., N is the number of atoms). The experimental data for plasmon energies are taken from [12] (neutral clusters) and [13,23] (charged clusters) and for SDP from [12,22]

	$\bar{\omega}$, eV		SDP, R^3	
Cluster	*exp.*	*SRPA*	*exp.*	*SRPA*
Na_8	2.59	2.66	1.77(3)	1.78
Na_{20}	2.67	2.80	1.68(10)	1.57
Na_{40}	2.72	2.68	1.61(3)	1.64
Na_{58}	-	2.83	-	1.41
Na_{92}	-	2.85	-	1.41
Na_{138}	-	2.91	-	1.37
Na_9^+	-	2.66	-	1.44
Na_{21}^+	2.68(1)	2.68	-	1.51
Na_{41}^+	2.62(1)	2.75	-	1.51
Na_{59}^+	2.8	2.85	-	1.39
Na_{93}^+	-	2.88	-	1.36
Na_{139}^+	-	2.94	-	1.34

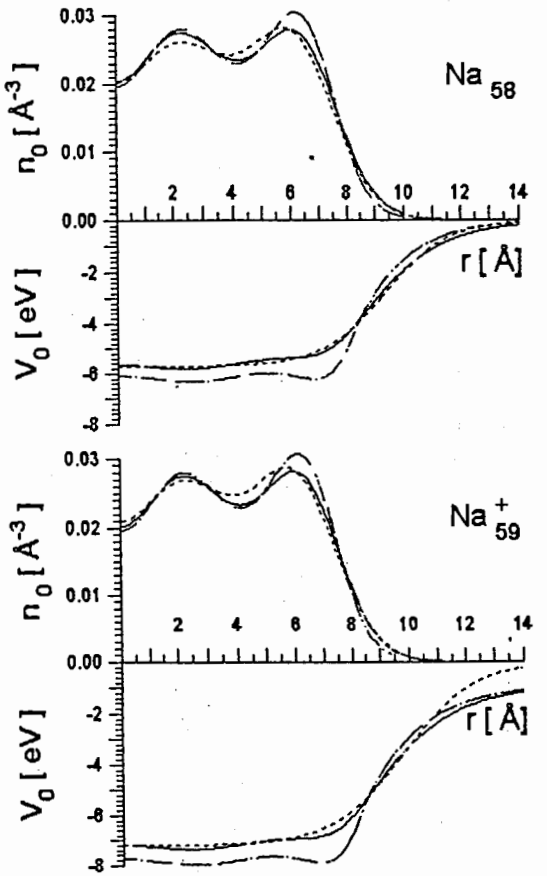

Figure 1. Ground state densities $n_0(r)$ and single particle potentials $V_0(r)$ in Na_{58} and Na_{59}^+ calculated with the diffused Kohn-Sham (**solid line**), sharp Kohn-Sham (**dashed line**) and Woods-Saxon (**dotted line**) single-particle schemes.

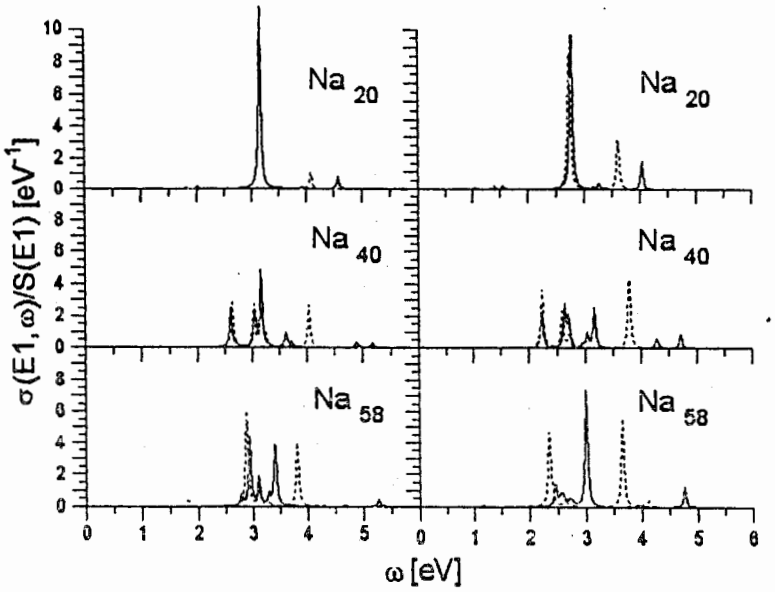

Figure 2. E1 strength functions calculated with (**solid line**) and without (**dotted line**) coupling with volume modes. The results obtained with the diffused (sharp) Kohn-Sham are given in the right (left) -hand side.

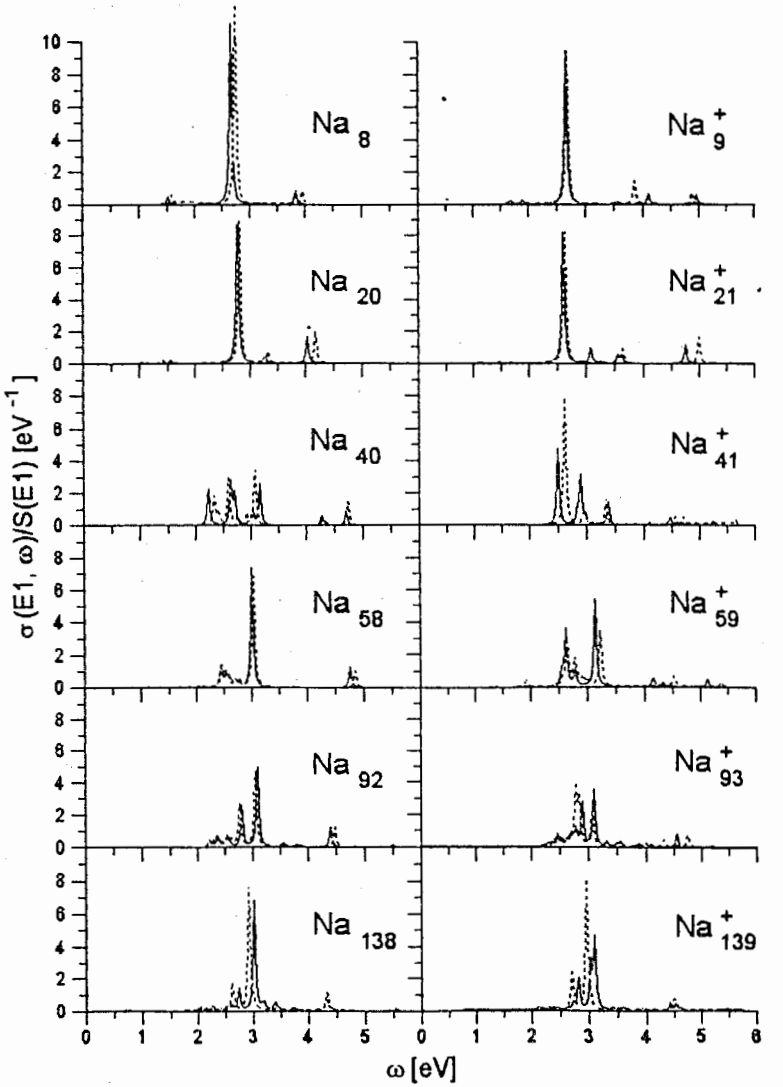

Figure 3. E1 strength functions calculated taking into account coupling with volume modes. The diffused Kohn-Sham (**solid line**) and Woods Saxon (**dotted line**) single-particle schemes are used.

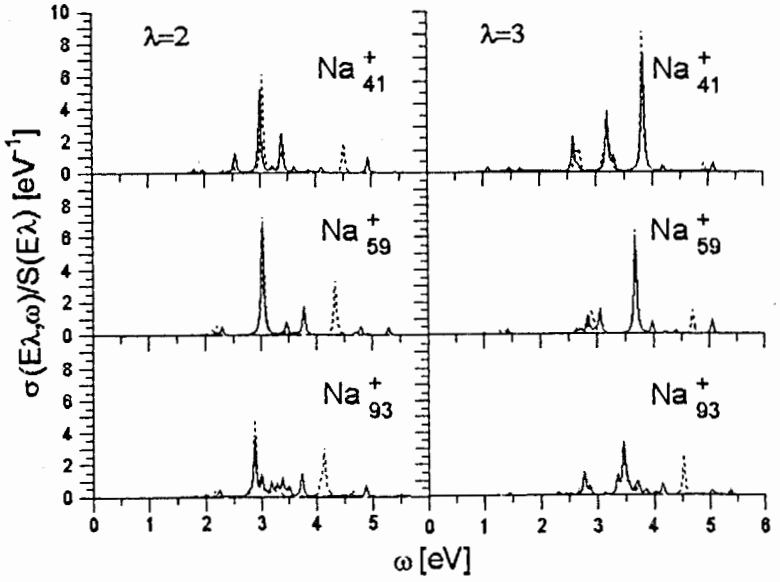

Figure 4. E2 and E3 strength functions calculated with **(solid line)** and without **(dotted line)** coupling with volume modes. The diffused Kohn-Sham is used.

4. Conclusions

The self-consistent schematic RPA has been generalized to take into account the coupling of surface and volume modes. Due to this coupling, the excess of the high-energy dipole strength is removed and thus a description of the dipole plasmon and static dipole polarizability is considerably improved. Good agreement with the experimental data is achieved. The predictions for E2 and E3 collective oscillations are given.

The present study proves the applicability of the separable approximation. The separable form of the residual interaction drastically simplifies the RPA calculations and thus can be quite useful for the description of $E\lambda$ excitations in deformed and very large MC.

The new sets of the Woods-Saxon parameters are proposed for neutral and singly charged sodium clusters. The calculations demonstrate good applicability of this phenomenological potential for the description of the dipole plasmon.

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