Optical spectra of hot alkali-metal clusters from the random-matrix model

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We show that the experimentally observed spectra of optical absorption of sodium cluster ions can be explained in the framework of the same random-matrix model, that has been employed earlier [Phys. Rev. Lett. **75**, 220 (1995)] for the ground-state properties of alkali-metal clusters. This approach reveals the effect of cluster symmetry ''on average'' on the optical-absorption profiles, describes their temperature dependence, and predicts the line shapes of two-photon absorption. [S0163-1829(96)06335-7]

Traditional models of quantum chemistry and condensed-matter physics work for metallic clusters of $N\sim 10$–1000 atoms are at the limits of their applicability. The central assumption of molecular physics, that is, adiabatic separation of the electronic and nuclear degrees of freedom, fails at $N\gtrsim 10$, when a typical distance between neighboring electronic terms $\Delta E(\text{a.u.})\sim 1/N$ becomes comparable or smaller than a typical nonadiabatic interaction $V_{\text{na}}(\text{a.u.})\sim\Lambda$, suggested by the Born-Oppenheimer parameter $\Lambda=(m_e/m_{\text{at}})^{1/4}\sim 1/10$. The concept of weakly interacting quasiparticles central to solid-state physics fails, in turn, for small clusters of $N\lesssim 1000$ atoms, when the mean free path of the electrons $l_f(\text{a.u.})\sim\Lambda^{-1}\sim 10$ exceeds a typical cluster radius $R(\text{a.u.})\sim N^{1/3}$, and the electron-phonon interaction no longer results in a homogeneous broadening of the excited electronic states. In particular, the optical absorption profiles calculated in the frameworks of the standard molecular[1] and solid-state[2] approaches for alkali-metal clusters of $N\sim 20$ atoms deviate considerably from the experimentally observed[3] line shapes, and this difference increases when the cluster size moves off the limits of applicability of the models.

In the present paper we show that a conceptually simple random-matrix model[4] fills the gap between consistent molecular and solid-state descriptions of the optical-absorption spectra for the alkali-metal clusters of $10<N<1000$ atoms. It not only yields the correct positions of the spectral lines, but also allows one to simulate the line shapes, and thereby reveal information about the structure of clusters hidden in the profiles of their optical absorption. Transformation of the optical spectra with an increase of temperature[5] finds its explanation as well. Moreover, the model allows one to find the two-photon line shapes.

Our approach is applicable to ensembles of vibrationaly excited clusters including different possible isomeric modifications. It involves, considering the problem in a basis of separable electronic and vibrational states. At finite temperatures each of the clusters has an individual electronic Hamiltonian $\hat{H}$ which depends on the particular vibrational state due to the electron-vibrational interaction. The model relies on the average Hamiltonian $\hat{H}_0$ of the ensemble and treats nonadiabatic deviations $\hat{V}$ of the individual Hamiltonians $\hat{H}$ from $\hat{H}_0$ as a random perturbation. We therefore consider the problem in two steps. For an ensemble of clusters of a given size N we first find the average Hamiltonian in framework of a reasonable model, and than we calculate the photoabsorption spectrum of the ensemble with the help of the transformation rule[6] for the spectra of quantum systems perturbed by a random matrix.

We take as an example the Na_{21}^{+} cluster ion, which has closed electronic shell structure, and therefore in the ground state it does not experience the spontaneous deformation resulting from the Jahn-Teller instability[7] of electronic clouds. In Fig. 1 we show the spectrum of exited one-electron–one-hole states calculated[8] with the help of the local-density method for a spherical jellium model in the random-phase approximation. This model suits our goal to find an ensemble-average Hamiltonian, since it ignores individual positions of atoms and considers the ionic cores ''on average'' as a positively charged background. It also provides the dipole matrix elements for the transitions among the states. For spherically symmetric clusters the representation in

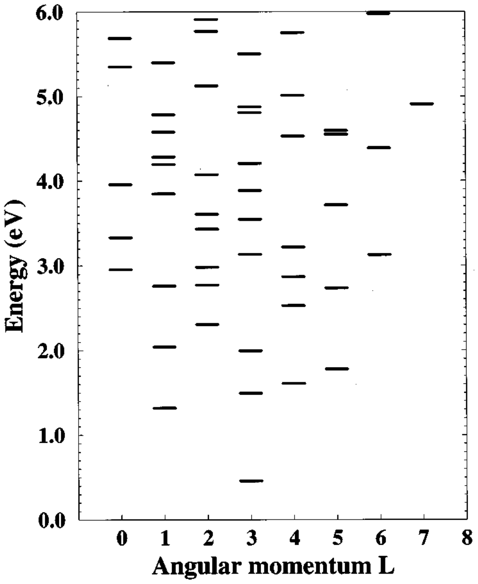

FIG. 1. Energy levels of Na_{21}^{+} cluster calculated in the local density and random phase approximation for the spherically symmetric jellium model with Wigner-Seitz radius $r_S=3.93$ a.u. Only the states corresponding to a single exited electron and a single hole have been taken into account. The number of the one-electron states chosen for the basis set ensures the convergency at the energy region essential for the optical absorption.

terms of the total angular momentum L and the correspondent magnetic quantum number M is the most convenient.

We note however, that even for the closed-shell clusters the mean Hamiltonian of the ensemble is not necessary spherically symmetric.[9] A residual molecular structure or a precursor of the crystalline planes of the bulk metal may affect the ''symmetry on average.'' This perturbation can originate both from the nonspherical shape of the cluster and from the Bragg scattering of electrons at the crystalline structure, which is also unisotropic. It mixes up the states with different L and M and lifts up the selection rules for optical transitions. We allow for these phenomena by adding the corrections

$$V_{\mathrm{un}}(\theta,\phi)=\sum_{LM}\left(\alpha c^{(\mathrm{el})}_{LM}+\beta c^{(\mathrm{th})}_{LM}+\gamma c^{(\mathrm{cu})}_{LM}+\delta c^{(\mathrm{ic})}_{LM}\right)Y_{LM}(\theta,\phi) \tag{1}$$

to the mean Hamiltonian of the spherical jellium model. Here $c^{(el)}_{LM}$, $c^{(th)}_{LM}$, $c^{(cu)}_{LM}$, and $c^{(ic)}_{LM}$ are the expansion coefficients of ellipsoid, tetrahedron, cube, and icosahedron over the spherical harmonics $Y_{LM}(\theta,\phi)$, respectively.[10] The coefficients α,β,γ, and δ determine the size of each of the perturbations. They have to be found from the experimental profiles of the spectral lines by comparing them with the line shapes calculated with the allowance of the temperature effect. We vary only one of these parameters and keep three other equal to zero; that enables us to determine the cluster symmetry ''on average.''

The effect of temperature transforms considerably the profiles of optical lines such that the positions and the oscillator forces of the individual transitions corresponding to the average Hamiltonian of a given symmetry cannot be resolved. However, they can be found from the line shapes, if we describe the thermal perturbation with the help of the random-matrix model. We start with the expression

$$\sigma(\omega)=\frac{\mathcal{E}^2}{\pi}\left\langle \mathrm{Im}\left\langle 0\left|\hat{d}\,\frac{1}{\hbar\omega-\hat{H}_0-\hat{V}-i0}\,\hat{d}\right|0\right\rangle\right\rangle_{\hat{V}} \tag{2}$$

for the ensemble averaged $\langle\cdots\rangle_{\hat{V}}$ probability of optical absorption from the ground electronic state $|0\rangle$, where $\hat{d}$ is the operator of dipole moment along the direction of electrical component $\mathcal{E}$ of the optical field.

The transformation rule[6] for the spectra of quantum systems perturbed by a random matrix suggests a simple, practical way to find the ensemble average Eq. (2),

$$\sigma(\omega)=\frac{\mathcal{E}^2}{\pi}\mathrm{Im}\left\langle 0\left|\hat{d}\,\frac{1}{\tilde{E}(\hbar\omega)-\hat{H}_0-i0}\,\hat{d}\right|0\right\rangle, \tag{3}$$

by replacing the energy of quantum $E=\hbar\omega$ by the renormalized energy $\tilde{E}(E)$, which is the continuous from $E=-\infty$ to $E=\infty$ solution of the nonlinear complex-valued equation

$$E=\tilde{E}+\langle\mathcal{V}^2\rangle\mathrm{Tr}\frac{1}{\tilde{E}-\hat{H}_0-i0}. \tag{4}$$

Apart from the discrete eigenstates, the trace operator also includes the second ionization continuum of the Na_{21} cluster. The lowest second continuum starts at $E_{ii}\sim5.6$ eV.

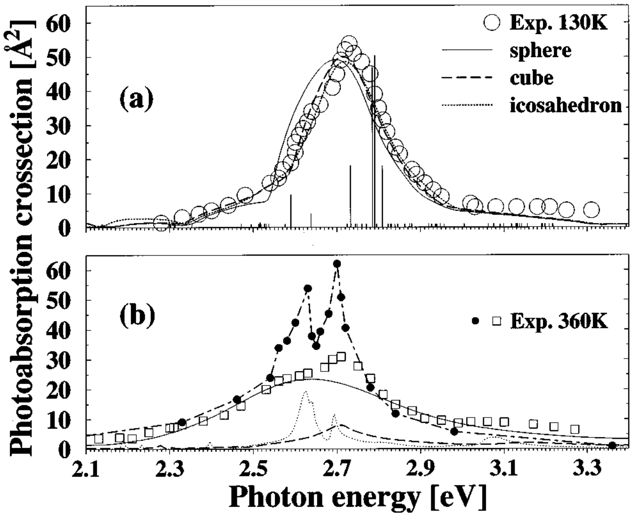

FIG. 2. (a) Experimental profile of the absorption line in Na_{21}^{+} at $T=130$ K from Ref. 11 (circles) and the profiles calculated for the same temperature for the of spherical ''on-average'' clusters (solid line), the cubic perturbation $\gamma=0.18$ eV (dotted line) and the icosahedral perturbation $\delta=0.12$ eV (dashed line). By ticks we show the positions of eigenstates and by vertical lines the correspondent cross-sections of photo absorption (not to scale) for the mean Hamiltonian $\hat{H}_0(cube)$ with $\alpha=\beta=\delta=0$; $\gamma=0.18$ eV. (b) The profile for evaporating ensemble at estimated temperature $T=360$ K of Ref. 11 (squares), and Ref. 12 (filled circles), and the simulated spectrum for the spherical jellium with cubic perturbation $\gamma=0.18$ eV (solid line). Photo absorption (not to scale) from the first electronically excited state suggested by the mean Hamiltonian $\hat{H}_0(cube)$ is shown for $T=50$ K (dotted line) and $T=150$ K (dashed line).

By $\langle\mathcal{V}^2\rangle$ we denote in Eq. (3) the mean-squared random coupling of electron terms. Earlier,[4] considering the properties of alkali-metal clusters in the ground electronic term, we have found the similar value $\langle V^2\rangle=(9\hbar^4/4r_S^4m_e^2N)\lambda T$, which gives the mean-squared coupling of one-electron states in terms of the cluster temperature T, with $\lambda=0.74\times10^{-5}(\mathrm{K}^{-1})$ for sodium. Now, dealing with random coupling of excited terms, we have to take into account that each excited one-electron state corresponds to $N-2$ possible locations of the hole in the N-atomic cluster ion, and therefore according to the sum rule the mean-squared matrix element of random coupling is $N-2$ times smaller for the electron terms as compared to that for the one-electron states. It immediately suggests the relation $\langle\mathcal{V}^2\rangle=(9\hbar^4/4r_S^4m_e^2N)\lambda T/(N-2)$ between the random coupling and the temperature.

In Fig. 2(a) we depict the absorption profiles of Na_{21}^{+} clusters—at temperature $T=130$ K calculated for the icosahedral on-average perturbation, Eq. (1), with $\delta=0.12$ eV and the cubic on-average perturbation with $\gamma=0.18$ eV—that have also been averaged over all possible orientations of the cluster with respect to the optical field polarization. With circles we show the experimentally observed[11] spectrum. The tetrahedral and elliptic perturbations move the absorption profile off the experimentally observed one. One can see that the icosahedral and cubic perturbations yield almost equally good agreement with the experimental data of Ref. 11 for the linear absorption in an ensemble of clusters at the temperature $T=130$ K. We note that the cubic symmetry corresponds to the crystalline structure of the bulk sodium, and the icosahedral symmetry might be favored by the liquid phase, where each atom has, on-average, five neighbors.[13]

In Fig. 2(b) we show the absorption profile of clusters at $T=360$ K calculated for the cubic perturbation and the spectrum of Na_{21}^{+} observed[11,12] in an evaporative ensemble with the estimated typical temperature $T=360$ K. One sees that the position and the width of the theoretical profile coincides with the experimental contour. However, a noticeable discrepancy among the theoretical profile and the experimental data obtained in slightly different experimental conditions of Refs. 11 and 12 still remains: As compared to the calculated line shape, both experimental profiles show additional absorption maxima, although the positions and the width of these maxima are different.

The mean Hamiltonian with cubic perturbation suggests an explanation of this additional absorption: it corresponds to the transitions from the lowest electronically excited state. This state originates from the sevenfold degenerate level with $L=3$ and $E\sim 0.4$ eV of the spherical cluster (see Fig. 1), split by the cubic perturbation. The lowest splitting component locates at $E\sim 0.11$ eV, and therefore it can be easily populated either as a result of thermal motion or in the course of accommodation of the laser-induced electronic excitation employed in the experiments for cluster heating. In the last case clusters cascade down over the electronic excited states and might be retained at the lowest one. In Fig. 2(b) we show the optical absorption from the lowest excited state calculated for two different temperatures. The difference in the experimental data may therefore be explained by the difference in temperature of the electronically excited species. It suggests an explanation of the difference, observed in two experiments Refs. 11 and 12, different preparation of the cluster ensembles results in different temperatures of the electrically excited clusters. Motivated by such good agreement between the theoretical and the experimental profiles of the linear absorption, we now consider two-photon absorption, since observation of such spectra could confirm or refute the theoretical assumptions and the numerical values of the constants $\alpha,\beta,\gamma,\delta$ employed for our calculations. Moreover, it may also provide a possibility to distinguish between the cubic and icosahedral symmetry on average, of the Na_{21}^{+} cluster ensemble.

Two-photon resonances in clusters can be of two different types. They can result in the creation of one electron-hole pair or yield two such elementary excitations. We concentrate here only on the two-photon absorption of the first type. Corresponding cross sections can be found from the matrix of dipole moments and the levels scheme, Fig. 1, of the mean Hamiltonian with the allowance of the correction of Eq. (1), provided one neglects the correlations of state densities in the ensemble of clusters. In this case we apply the transformation rule of Eq. (3) independently to each of the resonance denominators in the standard expression[14] for the two-photon transition probability, and obtain

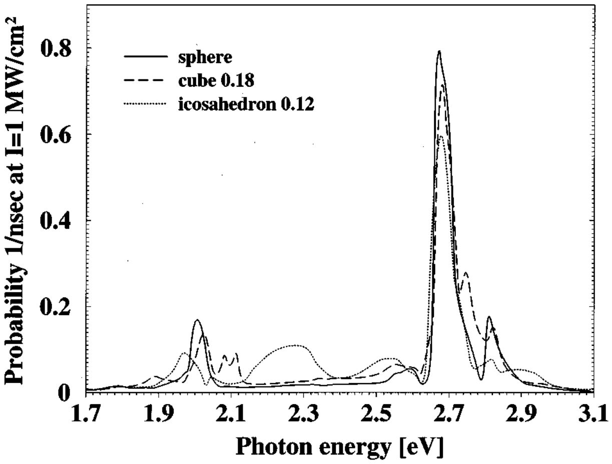

FIG. 3. Two-photon absorption at $T=130$ K corresponding to excitation of one electron-hole pair in the cubic (solid line), the icosahedral (dashed line), and the spherical "on average" cluster Na_{21}^{+} Absorption probability $\sigma^{(2)}(\omega)[\mathrm{sec}^{-1}]$ is normalized to the square of laser field intensity $I[MW/\mathrm{cm}^2]$.

$$\sigma_1^{(2)}(\omega)=\frac{\mathcal{E}^4}{\hbar^3\pi}\mathrm{Im}\left\langle 0\left|\hat{d}\frac{1}{\underset{\sim}{E}(\hbar\omega)-\hat{H}_0-i0}\hat{d}\frac{1}{\underset{\sim}{E}(2\hbar\omega)-\hat{H}_0-i0}\right.\right.$$
$$\left.\left.\times\hat{d}\frac{1}{\underset{\sim}{E}^*(\hbar\omega)-\hat{H}_0+i0}\hat{d}\right|0\right\rangle. \tag{5}$$

The main argument in favor of this approximation is a large difference between typical detunings from the resonance of intermediate levels contributing to the two-photon transition amplitudes and an energy distance at which the correlation of state densities becomes important: The last is of the order of the inverse density of states, whereas the first is of the order of the spectral width of the linear absorption.

In Fig. 3 we show the line shapes of two-photon resonances calculated for the icosahedral and cubic perturbations. We also show the two-photon resonance curve for the clusters that are spherically symmetric on average. The main contribution to the cross section results from the two-photon transitions to the states with $L=0$ and $L=2$ near the energy $E=4$ eV (see Fig. 1) that pass via the intermediate state $L=1$; $E\sim 2$ eV and the transitions to the states $L=0,2$ in the energy interval $E=5-6$ eV that have an intermediate resonance at the plasmon frequency.

We conclude by summarizing the main results. The random-matrix model allows one to calculate the optical-absorption profiles of hot metallic clusters of $N\sim 10$–1000 atoms at different temperatures, for which the nonadiabatic interactions of vibrational and electronic motions cannot be adequately taken into account by the standard methods of quantum chemistry and solid-state physics. It also suggests a way to extract the information hidden in this profile about the average symmetry of clusters originating from the residual molecular structure or the precursor of crystalline structure of metals. Comparison of the calculated two-photon line shapes with the results of the future femtosecond laser experiments will give an additional possibility to investigate the average symmetry of clusters and refine the models employed for the calculation of the "average" spectrum.

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$$V_S^{S'} = \int \frac{\psi_{n_e l_e}(r_1)\psi_{n_h l_h}(r_1)\psi_{n'_e l'_e}(r_2)\psi_{n'_h l'_h}(r_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\, d^3r_1 d^3r_2 - \frac{1}{2}\int V_{\mathrm{xc}}(r)\,\psi_{n_e l_e}(r)\,\psi_{n_h l_h}(r)\,\psi_{n'_e l'_e}(r)\,\psi_{n'_h l'_h}(r)\, d^3r \qquad (6)$$

of the states $S=|n_e,l_e,n_h,l_h\rangle$ and $S'=|n'_e,l'_e,n'_h,l'_h\rangle$, where by the factor 1/2 in front of the second integral we roughly allow for the fact that the excited electron usually is not surrounded by occupied states, and therefore it does not experience the exchange interaction, which affects only the motion of hole.

[9] For the influence of polyhedral symmetry on the classical plasma oscillations see M. Seidl and M. Manninen, Z. Phys. D **33**, 163 (1995).

[10] One finds these coefficients by taking several largest values $c_{L,M}^{(\mathrm{sym})}=\Sigma_k Y_{LM}^{*}(\theta_k,\phi_k)$, where k numerates foci of an ellipsoid or vertices of tetrahedron, cube, or icosahedron for $(\mathrm{sym})=(\mathrm{el})$, (th), (cu), or (ic), respectively.

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