Temperature effects on the optical absorption of jellium clusters

Z. Penzar,* W. Ekardt, and A. Rubio†
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, West Germany
(Received 21 February 1990)

Temperature broadening of the microscopically obtained optical absorption of open-shell clusters is studied with Na_{10} as an example. The method used is the time-dependent local-density approximation, combined with the coupling to the shape fluctuations of the cluster, both in the ground state and in the excited state. In sharp contrast to earlier studies by Pacheco and Broglia, the quantum nature of the fluctuations is fully taken into account. The obtained linewidth is in good agreement with recent experimental data of Knight and collaborators. The breakdown of the so-called plasmon-pole approximation is investigated in detail, and it is found that the reason for this is the fragmentation of the oscillator strength stored in the plasmon line, which is a genuine particle-hole effect *both* in closed-shell jellium clusters (Na_{20}) *and* in open-shell metal clusters (Na_{10}).

I. INTRODUCTION

It is well known that many of the electronic properties of clusters of the monovalent metals such as Na,K,Li and Cu,Ag,Au both in the neutral state and in the ionized one, can be successfully described by a relatively simple model, namely the jellium model.[1-3] Furthermore, both static properties, such as abundances and fragmentation properties, and dynamical properties, such as the optical absorption, can be obtained with reasonable accuracy within the relatively simple framework of density-functional theory. A good example for this is the optical absorption, which was calculated for the first time by one of us,[4] with the help of the time-dependent local-density approximation (TDLDA). The main result of this study was that the optical absorption of small Na clusters consists predominantly of a huge surface-plasmon line, which nearly exhausts the total oscillator strength. For this reason we investigated the accuracy of a much simpler approach—the so-called surface-plasmon-pole approximation,[5,6] within which the optical absorption consists exclusively in the excitations of the collective oscillations of the electrons against the jellium background. The theoretically predicted result,[4] that the absorption consists mainly of the excitation of surface plasmons, was later experimentally confirmed by Knight and collaborators.[7,8] This experimental finding demonstrated, convincingly, that the TDLDA is an excellent starting point for a first investigation of the optical absorption in metal clusters such as $(Na)_N$ $(2 \leq N \leq 41)$. However, there is an important exception of this general observation: The linewidth as determined within the pure TDLDA is completely wrong. The reason for this is the following: Small metal clusters formed by ultrasonic jet expansion are not really cold ($T=0$ K), but warm ($T \neq 0$ K), which means that their shape is not frozen, but fluctuating around the shape determined by minimizing the total energy at $T=0$ K.

Of course, for $T \neq 0$ K the other atomic vibration and isomerization modes in a cluster will also be excited (besides the shape fluctuation). However, the cluster-shape fluctuations will most strongly affect the photoabsorption cross-section frequencies: In monovalent metal clusters, already as small as $N=10$ (the example demonstrated in this work), the largest photoabsorption oscillator strength is stored in the electronic modes with a strong collective character, around the surface-plasmon resonances.[9-11] Charge-density oscillations associated with these collective modes are delocalized and spread over the whole surface of the cluster.[9] The frequency of these modes will only be sensitive to the overall changes in the global cluster shape, particularly to the quadrupolar shape oscillations, described by our spheroidal-jellium model.[3,11]

As demonstrated recently by Pacheco and Broglia,[12] these cluster-shape fluctuations result in roughly the experimentally observed linewidths. However, the model used by these authors assumes two serious simplifications.

(i) The surface-plasmon-pole approximation is used from the very beginning.

(ii) The effect of the shape fluctuation of the cluster is considered within classical statistical mechanics.

In the present work, we would like to improve on this model calculation, by taking into account the following two effects.

(a) Taking into account the fragmentation of the oscillator strength found microscopically by Ekardt,[9] Yannouleas *et al.*,[10] and Ekardt and Penzar,[11] which destroys the validity of the surface-plasmon-pole approximation for very small clusters $(Na)_N$, with $N \leq 41$.

(b) By taking into account that quite generally *small* clusters should exhibit a quantization of their shape fluctuations, which means that one should introduce wave functions and quantum statistics for a thorough calculation of this effect. Therefore the paper is organized as follows: In Sec. II the optical absorption is calculated in the spirit of Ref. 12, but *without* invoking any pole approximation: the particle-hole structure of the spectrum is taken fully into account and temperature effects are introduced via classical statistics. In Sec. III we present what should be a reference point for further investiga-

tions: The absorption is calculated by the microscopic TDLDA and the quantization of the shape fluctuations is fully taken into account. This yields a finite linewidth already at $T=0$ K, because of the zero-point oscillations, which is a *genuine quantum-mechanical effect.*

II. VALIDITY OF THE POLE APPROXIMATION

Microscopically, the cross section for single-photon absorption[9,11] is given by the imaginary part of the dynamical polarizability $\alpha(\omega)$,

$$\sigma(\omega)=\frac{4\pi\omega}{c}\mathrm{Im}\alpha(\omega) , \tag{1}$$

where $\alpha(\omega)$ for closed-shell clusters is discussed in detail in Ref. 9 and for open-shell clusters in Ref. 11. As the full application of the TDLDA results in a relatively cumbersome computer calculation[4] for $\alpha(\omega)$, one very often replaces $\alpha(\omega)$ by the plasmon-pole approximation:[5]

$$\alpha(\omega)=\tfrac{1}{3}R^3\frac{4\pi\bar{n}e^2/m}{\omega_s^2-\omega^2-i\omega\Gamma_s} , \tag{2}$$

where within the jellium model[1] we have

$$R=r_s N^{1/3} , \tag{3a}$$

$$\bar{n}=(\tfrac{4}{3}\pi r_s^3)^{-1} , \tag{3b}$$

where r_s is the Wigner-Seitz radius of the bulk metal for a cluster consisting of N atoms of a monovalent metal. Furthermore, the resonance frequency ω_s in Eq. (2) is given by [trivially, see Eq. (2)]

$$\omega_s^2=\frac{Ne^2/m}{\alpha(0)} , \tag{3c}$$

with $\alpha(0)$ the static polarizability. The width Γ_s in Eq. (2) is to be obtained microscopically—for instance, from the TDLDA.

However this "intrinsic" width is *not* to be confused with the "effective" width as observed in a real experiment. As noted by Pacheco and Broglia,[12] this effective width is mainly due to shape fluctuations around the minimum of the total-energy surface at given values of N and r_s. Therefore, Eq. (1) is to be replaced by

$$\sigma(\omega)\rightarrow\int d\tau_\delta\,\sigma(\omega,\delta)P(\delta,T) . \tag{4}$$

Here, δ is the parameter describing the cluster-shape fluctuation within the spheroidal model,[3,11] and $\sigma(\omega,\delta)$ is either that of Eq. (1), microscopic theory, or given by the pole approximation, Eq. (2), and $P(\delta,T)$ is the probability for the shape fluctuation, given by the total energy $E_t(\delta)$ and the partition function Z:

$$Z=\int d\tau_\delta\, e^{-E_t(\delta)/kT} \tag{5}$$

and

$$P(\delta,T)=e^{-E_t(\delta)/kT}/Z . \tag{6}$$

Expressions (1)–(6) constitute the so-called classical model, which neglects the quantum nature of the shape fluctuations around the optimum shape δ_0^i. We have cal-

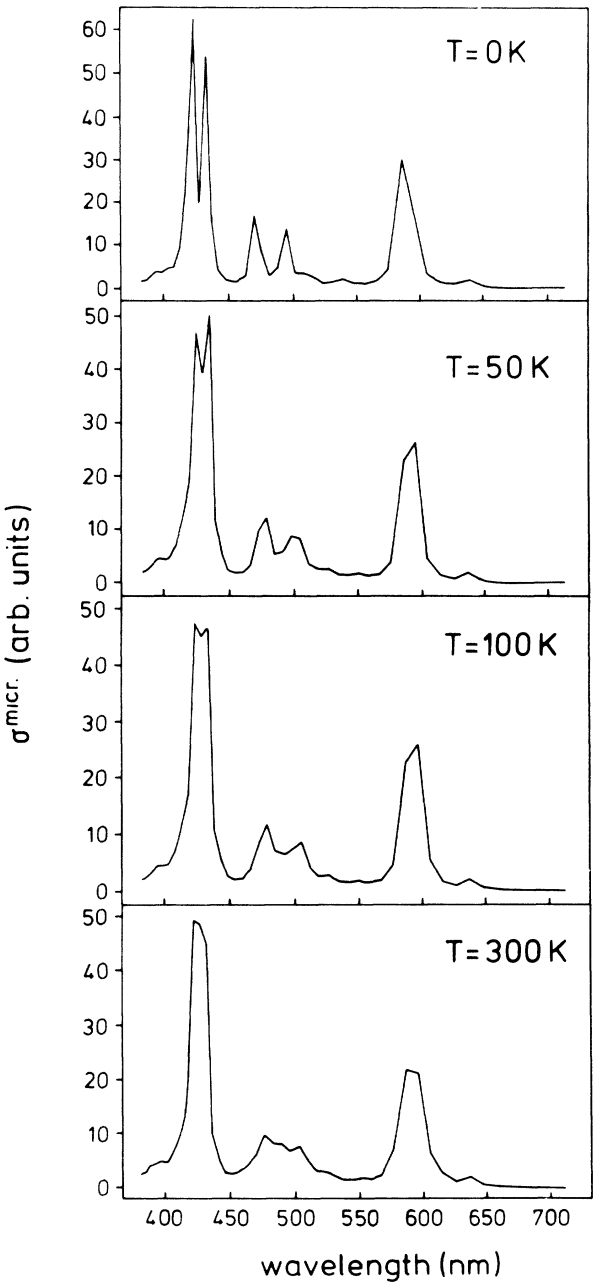

FIG. 1. Evolution of the photoabsorption cross-section spectrum with cluster temperature, T, for the Na_{10} cluster, obtained by using Eqs. (4)–(6). $\sigma(\omega,\delta)$ in Eq. (4) is obtained from the full microscopic TDLDA calculation in the self-consistent spheroidal jellium model (Ref. 11). Our temperature averaging requires the evaluation of the complete TDLDA photoabsorption spectra for many δ's [Eq. (4)], which is a very-computer-time-demanding task. Therefore, we calculated all the TDLDA spectra in the present paper by using only two spheroidal multipoles in the angular expansion of the TDLDA equations (Ref. 11), in contrast to Ref. 11, where the spectrum for only one δ is presented. This truncation brings a reduction of more than an order of magnitude in the computer time, preserving, on the other hand, all of the basic features, important for the results of this paper (static polarizabilities and δ-dependent fragmentation of the oscillator strengths stored in the plasmon lines, due to particle-hole effects).

culated Eq. (4) once microscopically, by using the full $\mathrm{Im}\alpha(\omega)$ for $\sigma(\omega,\delta)$ and using the total energy $E_i(\delta)$, in Eqs. (5) and (6), within the self-consistent spheroidal jellium model.[3] A typical result is given in Fig. 1 for Na_{10} at different temperatures, from $T=0$ to 300 K. We clearly see the fragmentation of the total oscillator strength already found earlier,[11] which destroys the validity of the plasmon-pole approximation. In order to make this point explicit, we give in Fig. 2 the optical absorption again with the use of the plasmon-pole approximation for $\sigma(\omega,\delta)$. Comparing Figs. 1 and 2 at *finite* temperatures, we clearly see that the fragmentation of the plasmon line itself is an important broadening mechanism. This clearly shows the breakdown of the plasmon-pole approximation (at least at finite temperatures).

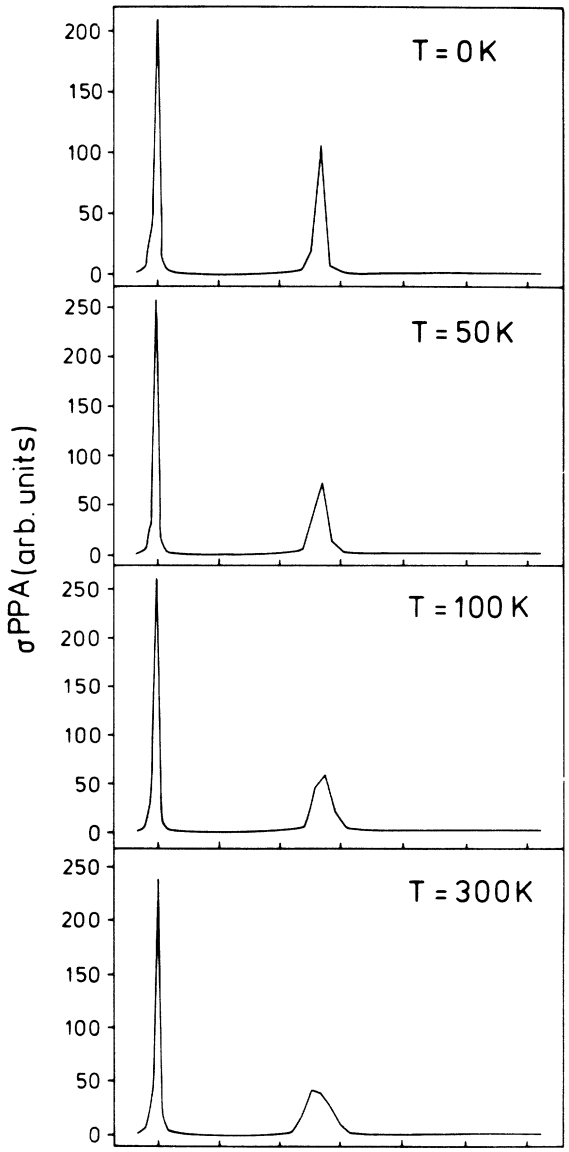

FIG. 2. Evolution of the photoabsorption cross-section spectrum with cluster temperature, T, for the Na_{10} cluster, obtained by using Eqs. (4)–(6). $\sigma(\omega,\delta)$ in Eq. (4) is obtained from the plasmon-pole approximation (PPA) for the spheroidal particle (Ref. 11): $\sigma^{\mathrm{PPA}}(\omega,\delta)=[4\pi\omega/(3c)]\mathrm{Im}[\alpha_z^{\mathrm{PPA}}(\omega,\delta)+2\alpha_\rho^{\mathrm{PPA}}(\omega,\delta)]$, with dynamical polarizabilities along z and ρ directions, $\alpha_i^{\mathrm{PPA}}(\omega,\delta)$ $(i=z,\rho)$, given by using Eq. (2), with the accompanying ω_i obtained from Eq. (3c), using for $\alpha(0)$ the *microscopically* (TDLDA) calculated direction-dependent static polarizabilities for every δ. The parameter Γ_i in Eq. (2) has been chosen to be 10^{-3} Ry, the same as the value of numerical damping (Ref. 4) in the TDLDA calculation.

III. QUANTUM THEORY OF THE LINEWIDTH

In this section we want to take into account the quantization of the shape fluctuations in the jellium cluster around its optimum distortion parameter, δ_0^i.[3,11] As the time scale of electronic transitions in the optical frequency region (energies approximately a few electron volts) is much shorter than the time scale of cluster-shape fluctua-

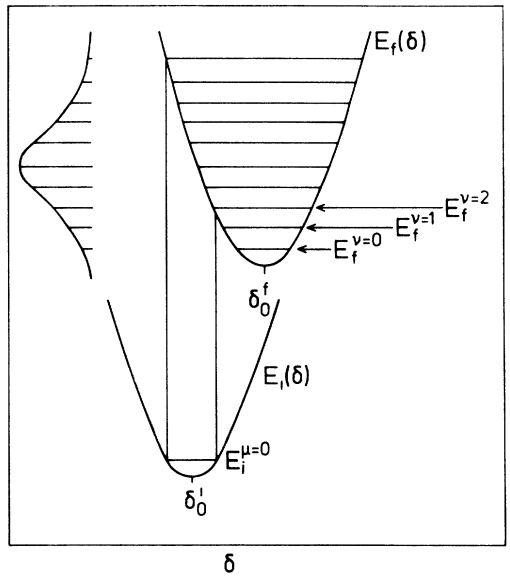

FIG. 3. Schematic presentation of the δ dependence of the ground-state energy curve, $E_i(\delta)$, and one of the excited-state energy curves, $E_f(\delta)$. Horizontal lines denote the positions of the total-energy eigenvalues (electronic plus vibrational). Due to the fact that the minima of $E_i(\delta)$ and $E_f(\delta)$ are at *different* δ's (δ_0^i and δ_0^f, respectively), which is a general situation, even for a cluster initially in the vibrational ground state of the curve $E_i(\delta)$ there is a non-negligible probability of optical transitions to various vibrationally excited states of the curve $E_f(\delta)$. In this case, the range of energies determining this effective broadening will roughly lie between the intersections of the curve $E_f(\delta)$ and the two vertical lines drawn. The corresponding distribution of excitation probabilities is schematically shown by the envelope in the upper left corner. Note that the vertical energy distance between the bottoms of the curves $E_i(\delta)$ and $E_f(\delta)$ is drawn unrealistically. The optical transition energies are typically of the order of about several electron volts, whereas the distances between vibrational energy levels belonging to one and the same adiabatic potential ($E_f^{\mu+1}-E_f^{\mu}$ or $E_f^{\nu+1}-E_f^{\nu}$) are of the order of about several multi-electron-volts.

tions (energies approximately a few milli-electron-volts), we can regard the ionic degrees of freedom as frozen during every electronic transition and use the Born-Oppenheimer approximation. That means we couple any electronic state $|\psi\rangle$ to the degree of freedom of shape fluctuations described by the wave function χ, by multiplying these two functions.

In order to obtain the ionic wave functions χ in this approximation, we first need to know the energies $E_i(\delta)$ and $E_f(\delta)$ as a function of δ, where $E_i(\delta)$ and $E_f(\delta)$ are the total cluster energies in the electronic ground state $|\psi_i(\delta)\rangle$ and in the particular electronically excited state $|\psi_f(\delta)\rangle$, respectively, assuming the frozen ionic background for every δ. The curve $E_i(\delta)$ is the same δ-dependent ground-state energy of the cluster encountered in the preceding section. The curve $E_f(\delta)$ is obtained in the following way: In the energy region of strong collective dipole resonances, in our case there are only bound-to-bound electronic transitions. Therefore, for every fixed cluster shape (fixed δ) there is a number of discrete excited states which can be reached by the dipole transition. The excitation energy from the electronic ground state to each of these states is just given by the position of the corresponding TDLDA peak. Let us denote by $\hbar\omega_f(\delta)$ the excitation energy from the electronic ground state $|\psi_i(\delta)\rangle$ to the electronically excited state $|\psi_f(\delta)\rangle$. The parametric δ dependence of $\hbar\omega_f(\delta)$ can be obtained from the TDLDA spectra for a sequence of δ's of interest. Now, the total cluster energy belonging to the electronically excited state $|\psi_f(\delta)\rangle$ can be obtained as

$$E_f(\delta)=E_i(\delta)+\hbar\omega_f(\delta) . \tag{7}$$

Next, we use the curves $E_i(\delta)$ and $E_f(\delta)$ as the adiabatic potential curves for ionic motion, approximated in the spirit of our model as the shape fluctuation of the incompressible spheroidal jellium continuum.[13] There are discrete vibrational states for the shape fluctuations of the spheroid in the adiabatic potentials $E_i(\delta)$ and $E_f(\delta)$, respectively. Let us call the ionic background wave functions corresponding to these states $\chi_i^\mu(\delta)$ ($\mu=0,1,2,\ldots$) and $\chi_f^\nu(\delta)$ ($\nu=0,1,2,\ldots$), and the corresponding total energies (vibrational and electronic) E_i^μ and E_f^ν (Fig. 3). This means that in contrast to the case of the classical treatment of the ionic background, we now obtain the photoabsorption cross section by replacing

$$\sum_f \int d\tau_\delta P(\delta,T)|\langle\psi_f(\delta)|H'|\psi_i(\delta)\rangle|^2 \frac{2\pi}{\hbar}\delta(E_f(\delta)-E_i(\delta)-\hbar\omega)$$
$$\rightarrow \sum_{f,\mu,\nu} P_\mu(T)\left|\int d\tau_\delta \chi_f^\nu(\delta)\chi_i^\mu(\delta)\langle\psi_f(\delta)|H'|\psi_i(\delta)\rangle\right|^2 \frac{2\pi}{\hbar}\delta(E_f^\nu-E_i^\mu-\hbar\omega) , \tag{8}$$

where

$$P_\mu(T)=\frac{e^{-E_i^\mu/kT}}{\sum_\mu e^{-E_i^\mu/kT}} , \tag{9}$$

and H' is the electron-photon–interaction operator.

We made three approximations in calculating expression (8).

(a) We used the harmonic approximation for the curve $E_i(\delta)$, expanding it around the minimum δ_0^i,

$$E_i(\delta)=E_i(\delta_0^i)+\tfrac{1}{2}I\omega_V^2(\delta-\delta_0^i)^2 , \tag{10}$$

where in our case I is the quadrupole moment of inertia of the jellium spheroid and ω_V the frequency of the spheroidal shape fluctuation.[13,14]

(b) Furthermore, following Mahan,[15] we linearized the δ dependence of the electronic excitation energies $\hbar\omega_f(\delta)$ around δ_0^i,

$$\hbar\omega_f(\delta)=\hbar\omega_f(\delta_0^i)+\left.\frac{d\hbar\omega_f(\delta)}{d\delta}\right|_{\delta=\delta_0^i}(\delta-\delta_0^i) . \tag{11}$$

(c) We approximated the matrix elements on the right-hand side of Eq. (8) as

$$\left|\int d\tau_\delta \chi_f^\nu(\delta)\chi_i^\mu(\delta)\langle\psi_f(\delta)|H'|\psi_i(\delta)\rangle\right|^2 \approx |\langle\psi_f(\delta_0^i)|H'|\psi_i(\delta_0^i)\rangle|^2 \left|\int d\tau_\delta \chi_f^\nu(\delta)\chi_i^\mu(\delta)\right|^2 . \tag{12}$$

All of these three approximations are legitimate, because in the range of δ's determined by the significant overlap of $\chi_i^\mu(\delta)$ and $\chi_f^\nu(\delta)$, Eqs. (10)–(12) are generally satisfied to a good extent. All of the thermal quantum shape-fluctuation effects on the photoabsorption cross section $\sigma(\omega,T)$ are now given through the *analytical* expression[15]

$$\sigma(\omega,T)=\sum_f \sigma_f(\omega_f(\delta_0^i),\delta_0^i)v_f(T,\omega) , \tag{13a}$$

where

$$v_f(T,\omega)=e^{-g[2N(T)+1]}\sum_{l=-\infty}^{+\infty} I_l(2g\{N(T)[N(T)+1]\}^{1/2})e^{l\hbar\omega_V/2kT}\delta(\omega_f(\delta_0^i)+(l-g)\omega_V-\omega)\ , \tag{13b}$$

with

$$g=\left[\frac{d\hbar\omega_f(\delta)}{d\delta}\bigg|_{\delta=\delta_0^i}\right]^2\Big/(2\hbar I\omega_V^3),\quad N(T)=(e^{\hbar\omega_V/KT}-1)^{-1}\ , \tag{13c}$$

I_l the Bessel function as defined in Ref. 16, and $\sigma_f(\omega_f(\delta_0^i),\delta_0^i)$ the height of the fth peak in the photoabsorption cross section at the frequency $\omega_f(\delta_0^i)$. In fact, our treatment of the influence of cluster-shape fluctuations on the effective photoabsorption width [Eqs. (13a)–(13c)] is the same as that recently used by Bertsch and Tománek,[13] with two important differences: Bertsch and Tománek use crude approximations for calculating both the ground-state energy $E_i(\delta)$ and the excited-state energies $E_f(\delta)$ (using the plasmon-pole approximation and neglecting all particle-hole–pair effects), whereas we calculate both functions microscopically and self-consistently.

In Fig. 4 we show the photoabsorption spectra for the same temperature sequence as in Fig. 1, just this time by considering the quantum nature of the cluster-shape fluctuations, via formulas (13a)–(13c). We immediately see that the consideration of the quantum nature of cluster-shape fluctuations considerably enhances the effective width of the photoabsorption spectral structures. The most significant difference arises, of course, for low cluster temperatures ($T\rightarrow 0$ K). Whereas the spectrum in Fig. 1 for $T=0$ K consists of well-separated lines, the corresponding spectral structures in Fig. 4 exhibit effective broadening, due to the zero-point quantum shape fluctuations.[17] This means that for clusters as small as $N=10$ used in the experiments[7,8] this broadening will be present *even if it were possible to produce extremely cold cluster beams.* This reasoning will also be qualitatively valid for the whole range of Na cluster sizes for which the photoabsorption has been measured so far ($N\leq 20$). For larger clusters, these broadening effects will become less important, scaling roughly as $\sim N^{-1/3}$, as estimated by Bertsch and Tománek.[13]

Typical estimated cluster temperatures in supersonic-beam experiments[2,9] are ≈ 300 K. The full width at half maximum (FWHM) of the two strongest peaks in Fig. 4 are $\Gamma=0.22$ eV for the high-energy (low-wavelength) peak and $\Gamma=0.19$ eV for the low-energy peak. The ratios of these FWHM's to $\omega_{\max}$, the frequency at the corresponding peak maximum, are 7.6% and 8.8% for the high- and low-energy peaks, respectively. This is in fair agreement with the rough estimate of the experimental values ($<15\%$),[8] especially if one takes into account that our model allows for the cluster-shape fluctuation only along one axis (spheroidal model instead of ellipsoidal model). Another non-negligible shape fluctuation, normal to the spheroidal axis, will contribute to the further broadening of the effective linewidth, presumably bringing our result closer to experiment.

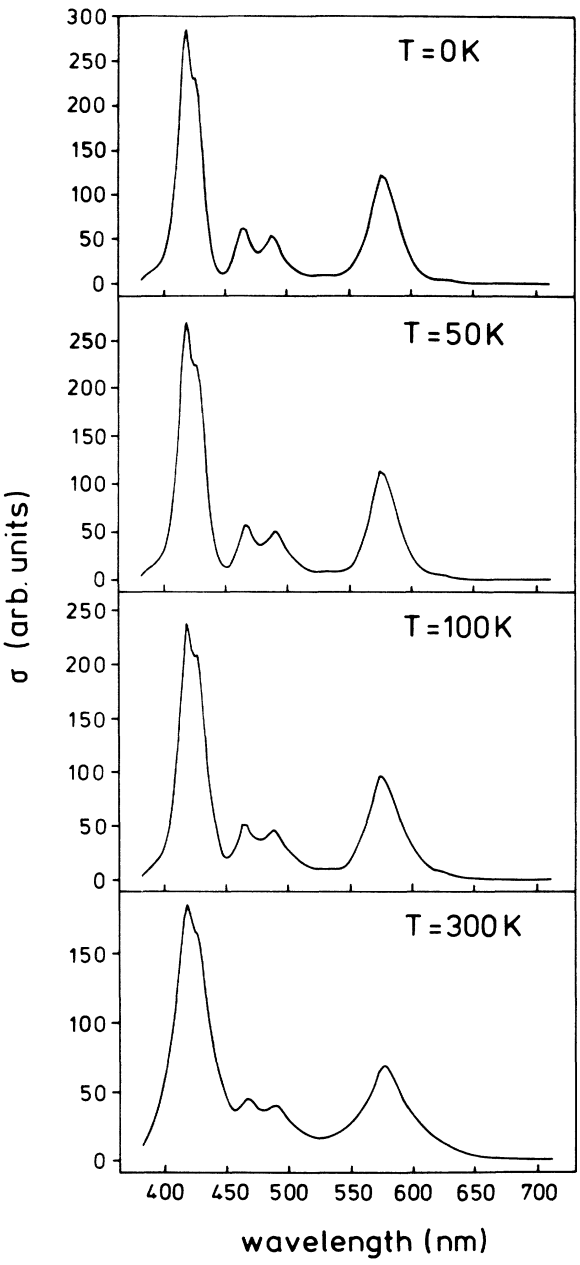

FIG. 4. Evolution of the photoabsorption cross-section spectrum with cluster temperature, T, for the Na_{10} cluster, by considering the quantum nature of cluster-shape fluctuations, obtained by using the results from the TDLDA-calculated spectra in Eqs. (13a)–(13c).

ACKNOWLEDGMENTS

We wish to express our thanks to Professor Elmar Zeitler for his continuing interest and support. This work was supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) through the Schwerpunkts Projekt:Physik anorganischer Cluster. One of us (A.R.) acknowledges a grant from the Universidad de Valladolid.

---

*On leave of absence from the Ruđer Bošković Institute of Physics of the University of Zagreb, P.O. Box 304, YU-41001 Zagreb, Croatia, Yugoslavia.

†Permanent address: Departamento de Fisica Teórica, Universidad de Valladolid, E-47011 Valladolid, Spain.

[1]W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[2]W. A. de Heer, W. D. Knight, M. Y. Chou, and M. L. Cohen, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1987), Vol. 40.

[3]W. Ekardt and Z. Penzar, Phys. Rev. B **38**, 4273 (1988); Z. Penzar and W. Ekardt (unpublished).

[4]W. Ekardt, Phys. Rev. Lett. **52**, 1925 (1984).

[5]W. Ekardt, D. B. Tran Thoai, F. Frank, and W. Schulze, Solid State Commun. **46**, 571 (1983).

[6]G. Bertsch and W. Ekardt, Phys. Rev. B **32**, 7659 (1985).

[7]W. A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Châtelain, and W. D. Knight, Phys. Rev. Lett. **59**, 1805 (1987).

[8]K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, Phys. Rev. B **40**, 5417 (1989).

[9]W. Ekardt, Phys. Rev. B **31**, 6360 (1985).

[10]C. Yannouleas, R. A. Broglia, M. Brack, and P. F. Bortignon, Phys. Rev. Lett. **63**, 255 (1989).

[11]W. Ekardt and Z. Penzar (unpublished).

[12]J. M. Pacheco and R. A. Broglia, Phys. Rev. Lett. **62**, 1400 (1989).

[13]G. F. Bertsch and D. Tománek, Phys. Rev. B **40**, 2749 (1989).

[14]G. F. Bertsch, Nucl. Phys. A **249**, 253 (1975).

[15]G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981), Sec. 4.3.

[16]*Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1964).

[17]Formulas (13a)–(13c), in principle, also give a spectrum, consisting of discrete lines—however, at a separation of the order of cluster vibrational energies (approximately several milli-electron-volts). In all of our TDLDA numerical calculations, we included the "numerical damping," $\Delta = 10^{-3}$ Ry (=0.0136 meV). This numerical damping is generally sufficient to distinguish between various electronic spectral lines, but not to resolve the vibrational lines. As the experimental resolution in cluster photodepletion experiments (Refs. 7 and 8) is not higher, the effect of quantum vibrational states will bring in an effective broadening and smearing in the experimental spectra, as in Fig. 4.