Photoabsorption cross sections of the alkaline-earth-metal elements under strong interaction conditions*

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The strong interatomic interaction effects on photoabsorption cross sections of a private atom have been interpreted by the contribution of both the real and imaginary parts of atomic polarizability in the present work. Some unresolved differences between the photoabsorption cross sections of isolated atoms and those of condensed atoms, especially near thresholds and resonances, probably could be interpreted by the competition between the imaginary and real parts of atomic frequency-dependent polarizabilities.

Keywords: condensed-phase photoabsorption, complex polarizability, alkaline-earth-metal elements

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1. Introduction

The photoabsorption cross sections of atoms and molecules are only dependent on the imaginary part of polarizability in the famous and fundamental expression.[1] This expression is accurate enough for atoms in isolated or ideal gas states. However, is only the imaginary part of polarizability enough for describing photoabsorption cross sections in condensed phase or under strong interatomic interaction conditions? Undoubtedly it is not enough. The real part of polarizability will contribute some characteristic structures to photoabsorption cross sections under these strong interatomic interaction conditions. However, almost no work has been done to study the influence of the real part on photoabsorption cross sections due to the absence of the real part in the famous expression. In the present work, an alternative scheme has been suggested to explain the different characteristic structures of photoabsorption cross sections between isolated and condensed atoms. The contributions of the real and imaginary parts to the characteristic structures of photoabsorption cross sections can be considered simultaneously by our previous alternative expressions.[2−4]

The study of the influence of interatomic interactions on photoabsorption cross sections of the atoms in a condensed environment or under high density, high temperature conditions has always been one of the main aims of condensed matter physics and chemical physics.[5−11] Understanding the relationship between the macroscopic electromagnetic responses of matter observed in experiments and microscopic properties such as photoabsorption cross sections of isolated atoms, and identifying the influence of the state of aggregation on the observable microscopic properties still present challenges.[7,9] The photoabsorption cross sections of the condensed atoms are usually quite different from the isolated ones, especially in the energy regions near thresholds or resonant structures. These environmental effects termed, for example, the condensed matter extended X-ray absorption fine-structure (EXAFS) or X-ray absorption near-edge spectroscopy (XANES) have been studied considerably for several decades.[12] However, quantitative analysis of these local structures is not fully developed and still remains a challenge. In the present work, another view has been raised for the first time, as far as we know, to interpret these different structures in photoabsorption cross sections between isolated and condensed atoms quantitatively. The variation of the photoabsorption cross sections of atoms from the isolated to condensed states can be represented by the competition between the imaginary and real parts of atomic frequency-dependent polarizabilities. The contributions of the real and imaginary parts

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of polarizability on photoabsorption cross sections will be quite different under different conditions. For photoabsorption cross sections of the atom in dilute or ideal gas, the characteristic structure of the imaginary part of polarizability is evident and the character of the real part is absent. While for the condensed atoms with very strong interatomic interactions, the real part of polarizability becomes more important and both the characteristics of the real and imaginary parts have appeared. In these condensed conditions, the contributions of both the real and imaginary parts should be taken into account and the general real-and-imaginary-parts-dependent expression[4] should be used.

2. Polarizability-dependent photoabsorption cross section

Usually, the photoabsorption cross sections $\sigma_{\rm i}(\omega)$ of isolated atoms can be calculated easily by the famous expression[1]

$$\sigma_{\rm i}(\omega) = \frac{4\pi\omega}{c}\zeta = \frac{4\pi\omega}{c}{\rm Im}(\alpha), \tag{1}$$

where ζ is the imaginary part of the frequency-dependent polarizability $\alpha(\omega)(=\eta + {\rm i}\zeta)$ of the isolated atoms; ω and c are the photon energy and the light velocity, respectively. In Eq. (1), the photoabsorption cross section relates only to the imaginary part of polarizability and independent of the real part and only represents the property of an isolated atom. This expression is the result of the first order approximation in a series expansion of the polarizability in an ideal gas model.[1] The more strict expression has been given previously[2−4] and has shown that the photoabsorption cross section will be dependent on not only the imaginary part but also the real part of polarizability. Due to the very weak interatomic interactions in ideal gas or dilute gas, all higher power terms with order ≥ 2 in series expansion are small enough and can be neglected at all. However, as the interatomic interactions become stronger and stronger, these higher terms should be taken into account and the real part of polarizability will then contribute to photoabsorption cross sections more and more. The influence of the surrounding atomic interactions with the photo-ionized atom on the photoabsorption cross sections can be easily investigated using the more general expression[2−4]

$$\sigma(\omega) = \frac{1}{2\sqrt{2}\pi N\zeta}\sqrt{\sqrt{\epsilon'(N;\eta,\zeta)^2 + \epsilon''(N;\eta,\zeta)^2} - \epsilon'(N;\eta,\zeta)} \times \sigma_{\rm i}(\omega). \tag{2}$$

In Eq. (2), $\sigma(\omega)$ represents the cross section of the atoms embedded in some condensed matter, while $\sigma_{\rm i}(\omega)$ represents the cross section of the same atoms which are isolated or in ideal gas. N and $\epsilon(N;\eta,\zeta)(=\epsilon'(N;\eta,\zeta) + {\rm i}\epsilon''(N;\eta,\zeta))$ are the number density and the dielectric tensor of condensed matter, respectively. In this alternative expression of photoabsorption cross sections, the contributions of the real and imaginary parts of polarizability could be taken into account equivalently. The competition between the real and imaginary parts and the evolution of the photoabsorption cross sections with the real and imaginary parts can be represented by the number density, which represents the strength of the interatomic interactions.

At present, the accurate photoabsorption cross section $\sigma_{\rm i}(\omega)$ of an isolated atom can be easily obtained. One direct way to obtain a photoabsorption cross section of the isolated atom is from the famous atomic photoabsorption database.[12] The imaginary part ζ of the polarizability can be calculated from Eq. (1)

$$\zeta(\omega) = \frac{c}{4\pi\omega}\sigma_{\rm i}(\omega). \tag{3}$$

Then, performing a Kramers–Kronig transformation, one can obtain the real part η of the frequency-dependent polarizability from the known $\sigma_{\rm i}(\omega)$[2−4]

$$\eta(\omega) = \frac{c}{2\pi^2}\,{\rm P}\int_0^\infty \frac{\sigma_{\rm i}(\xi)}{\xi^2 - \omega^2}\,{\rm d}\xi, \tag{4}$$

where P represents the Cauchy principal part and ξ is the photon energy. Then the dielectric tensor can be calculated using some local field models such as the famous Onsager model or the direct reaction field models.[9−11] For example, in the Onsager model, the real part ϵ' and the imaginary part ϵ'' of the dielectric function ϵ can be calculated from the expression

$$\epsilon = 1 + \frac{3\epsilon \times 4\pi N\alpha}{2\epsilon + 1 - 2\alpha/r^3(\epsilon - 1)},$$

where r is the radius of the Onsager cavity. Then the cross sections can be calculated reasonably and the accuracy of the results is mostly affected by the accuracy of the local field models. The more correct the model of the electric susceptibility for the condensed matter is, the more accurate the photoabsorption cross sections obtained from the present expressions will be. In the present work, the influence of the macroscopic local field effects on the photoabsorption cross sections has been represented by the famous Onsager model. Obviously, the photoabsorption cross sections in condensed phases are strongly dependent on the values of the number density N and the radius of the Onsager cavity. However, in the present work, focus has been placed on the evolvement of the characteristic structures of photoabsorption cross sections from the imaginary part to the real part of polarizability. For each condensed condition, the number density and the cavity radius can be taken as some constants. As a rule, these constant values will not influence qualitatively the variation of law of the photoabsorption cross sections with the real and imaginary parts of polarizability. In the present work, in order to simulate the strong interatomic interaction conditions, the values of the number density and the cavity radius have been taken to be $N \sim 10^{-2}a_0^{-3}$ and $r \sim 3a_0$, respectively.

3. Calculation and Discussion

In order to demonstrate the evolution of the photoabsorption cross sections, especially near thresholds or resonant structures, with the real and imaginary parts of atomic polarizability, the theoretical calculations have been performed on the alkaline-earth-metal atoms. This is because almost all of the relationships of the real and imaginary parts of polarizability appear in these alkaline-earth-metal atoms, as shown in Fig. 1. Using the accurate experimental photoabsorption cross sections[12] of these isolated alkaline-earth-metal atoms, the imaginary parts of the frequency-dependent polarizabilities over a wide energy interval from 30 eV to 30000 eV can be obtained using Eq. (3). The energy interval is wide enough to accurately perform the infinite Kramers–Kronig transformation in order to determine the real part of polarizability using Eq. (4). Performing the Kramers–Kronig transformation for this wide energy region, 30 eV–30000 eV, will guarantee the obtained real part of polarizability in 30 eV–500 eV region to be sufficiently correct. Then, the subsequent calculation procedures cannot be strongly influenced by the integral instability of the Kramers–Kronig transformation. Detail of the calculation procedure can be found in previous works.[2−4] In the present work, only the photon energy 30 eV–500 eV region is studied, and the real and imaginary parts of polarizability in this region are shown in Fig. 1.

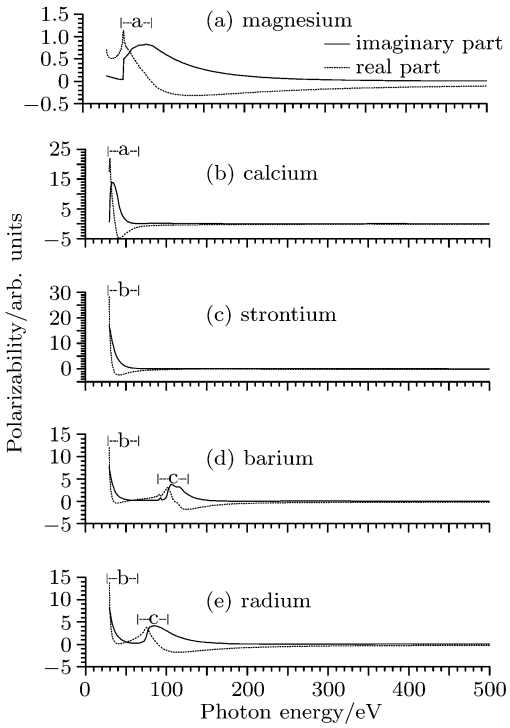


Fig. 1. The real and imaginary parts of the polarizabilities of the isolated alkaline-earth-metal atoms calculated from experimental photoabsorption cross sections.

Actually, the variation of the photoabsorption cross sections with number density represents the transformation of the contributions from the imaginary part to the real part. The competition between the imaginary and real parts of the atomic frequency-dependent polarizabilities occurred in the evolution of the photoabsorption cross sections from the isolated to the condensed atoms. The different relations between the real and imaginary parts of polarizability will give different evolution processes of the photoabsorption cross sections with interatomic interactions. In the energy region shown in Fig. 1, three kinds of relations between the real and imaginary parts of these alkaline-earth-metal atomic polarizabilities have appeared, which have been marked by the letters a, b and c, respectively. The suddenly raised structure of the imaginary part in the threshold region with a broad maximum peak following it can give a very sharp peak of the real part in the energy regions

marked by letter a for atomic Mg and Ca. Another threshold relation, marked by the letter b for atomic Sr, Ba and Ra, will represent another relationship of the real and imaginary parts. The third relationship represents a resonant structure marked by the letter c for atomic Ba and Ra. The amplitude of the interatomic interaction can be represented by the magnitude of the number density of the system in the Onsager model. The lowest number density represents the ideal gas or dilute gas condition, while the highest number density represents the very strong interatomic interaction environment. The extent of the difference between the real and imaginary parts will determine the different variations of the photoabsorption cross sections with number density. The influence of the real and imaginary parts of polarizability on the photoabsorption cross section is particularly evident near thresholds or resonances.

The evolution of the photoabsorption cross section of atomic Mg with number density is shown in Fig. 2(a). The different influences of the real and imaginary parts on the photoabsorption cross sections can be observed by comparing them with Fig. 1(a). In the 45 eV–150 eV energy region, as the number density increases, the peak of the real part at about 50 eV will appear more and more clearly in the photoabsorption cross sections. The influence of the real part on photoabsorption cross sections is more important for Mg even in low number density conditions. One can suggest that in some condensed conditions, some unresolved peaks in photoabsorption cross sections might be induced by the real part of polarizability, as shown in Fig. 2(b). The greater the difference between the real and imaginary parts is, the clearer the characteristics of the real part in the photoabsorption cross sections will be. We can conclude that the large difference between the real and imaginary parts of polarizability will cause the different behaviour of photoabsorption cross sections in low and high number density regions.

The real and imaginary parts of the polarizability of atomic calcium shown in Fig. 1(b) also have the same relations in the 90 eV–150 eV region as that of Mg in the 45 eV–150 eV region. The variation of the photoabsorption cross sections with number density in the 30 eV–60 eV region shown in Fig. 3 have similar characteristics to the variation in the 45 eV–150 eV region of Mg. The photoabsorption cross sections were mainly influenced by the imaginary part in small number density conditions and the real part in the large number density region. In Fig. 3, for low number densities, the photoabsorption cross sections have the same characteristics as the imaginary part of polarizability shown in Fig. 1(b). However, as the number density increases to a higher number, more and more characteristics of the real part will be shown in the photoabsorption cross sections. In a high number density region or in condensed matter, some peaks, which do not exist in the photoabsorption cross sections of the isolated atom, will appear due to the contribution of the real part of polarizability.

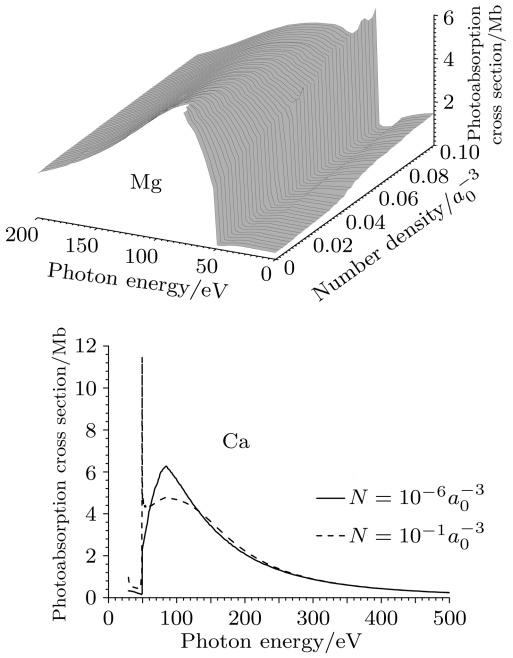


Fig. 2. Photoabsorption cross section versus photon energy for different N. The extent of the difference between the real and imaginary parts determines the different variations of photoabsorption cross sections with number density near the thresholds. The influence of the real part of polarizability on the photoabsorption cross section is evident in strong interatomic interaction conditions.

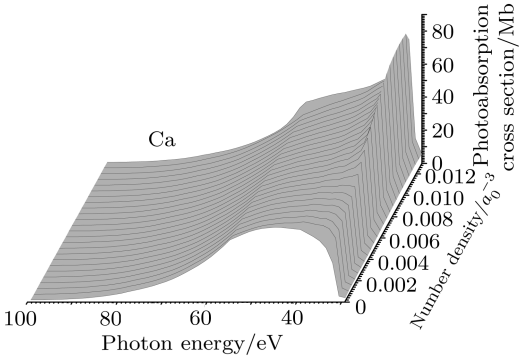


Fig. 3. Photoabsorption cross section versus photon energy and number density for Ca. In the high number density region, some peaks that do not exist in the photoabsorption cross sections of the isolated atom will appear due to the contribution of the real part of polarizability.

The transformation of the contributions from the imaginary part to the real part of polarizability on the photoabsorption cross sections near the threshold energy region is shown more clearly in Fig. 1(c) and Fig. 4 for atomic Sr. In the energy region larger than 90 eV, the real and imaginary parts of polarizability are almost identical and both convergent to zero. However, the real part has behaves differently from the imaginary part of polarizability in the 40 eV–90 eV energy region.

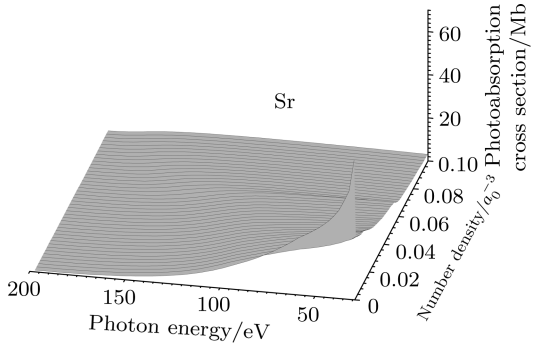


Fig. 4. Same as Fig. 3 but for Sr. The different behaviour of photoabsorption cross sections near the threshold can be interpreted by the competition between the imaginary and real parts of atomic frequency-dependent polarizability.

This simple characteristic of polarizability of Sr will show the threshold effect more clearly. Similar relations between the real and imaginary parts for atomic Ba and Ra in their threshold energy region are shown respectively in Fig. 1(d) and Fig. 1(e). The same relations will make the evolution of the photoabsorption cross sections of atomic Sr, Ba and Ra more similar, as shown in Fig. 4, Fig. 5(a) and Fig. 5(b) in the threshold energy region, respectively. As the number density increases, shown in Fig. 4 in 40 eV–90 eV, Fig. 5(a) in 40 eV–50 eV and Fig. 5(b) in 40 eV–50 eV, respectively, the photoabsorption cross sections are mostly determined by the imaginary part shown in Fig. 1(c), Fig. 1(d) and Fig. 1(e), respectively, marked by the letter b in the low number density initially. As the number density continues to increase to higher values, the contribution of the real part becomes more and more important and will be counteracted with the imaginary part. Therefore, the photoabsorption cross sections become increasingly small. Finally, the photoabsorption cross sections will tend to a constant and no longer vary with the energy in this energy region. These threshold effects can then be seen more clearly for atomic Sr, Ba and Ra in the threshold energy region, respectively, by comparing them with the relations of the real and imaginary parts of polarizability of atomic Mg and Ca in the 100 eV–150 eV, approximately 50-eV and approximately 35-eV energy regions, respectively, where the real part is sharper and larger than the imaginary part. For atomic Ba and Ra in the 75 eV–150 eV and 60 eV–150 eV energy regions, the shape of the real and imaginary parts is almost equivalent and the amplitude is almost equivalent. Almost the same amplitude of the real and imaginary parts will make the resonance of photoabsorption cross sections more broad in higher number density conditions due to the contribution of the real part of polarizability.

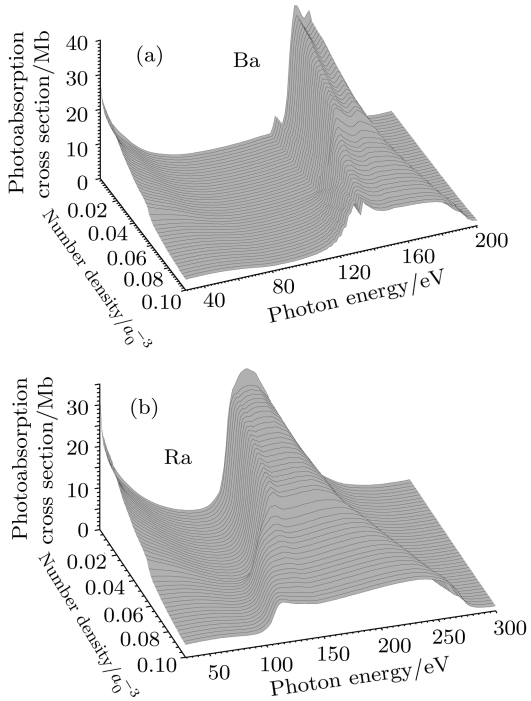


Fig. 5. Same as Fig. 3 but for Ba (Fig. 5(a)) and Ra (Fig. 5(b)). The almost identical amplitude of the real and imaginary parts will make the resonance of photoabsorption cross sections broader in higher number density conditions due to the contribution of the real part of polarizability.

4. Conclusion

The influence of the real and imaginary parts of atomic polarizabilities on photoabsorption cross sections in some condensed phases with strong interatomic interactions have been studied systematically in the present work. Some unresolved structures near thresholds or resonances in condensed photoabsorption spectra could be interpreted by the influence of the real part of atomic polarizability. In the conditions with weak or no interatomic interactions, the photoabsorption cross sections of atoms are mainly

determined by the imaginary part of atomic polarizability. The contribution of the real part of the polarizability to photoabsorption cross sections is small enough to be neglected. Therefore, only the characteristics of the imaginary part have been represented in the photoabsorption cross sections. However, as the interatomic interactions gradually increase, both the real and imaginary parts of atomic polarizability begin to influence the photoabsorption cross sections and the characteristics of the real part becomes more and more evident although the characteristics of the photoabsorption cross sections are still mainly determined by the imaginary part. When the interatomic interactions are strong enough, the photoabsorption cross section has then been determined by the real part.

In the present work, one of the conclusions is that the contribution of the real part of polarizability may introduce some extra peaks in the photoabsorption cross sections, especially near threshold and resonant structure regions. The competition between the imaginary and the real parts of atomic polarizability could probably explain some differences of the photoabsorption cross sections between isolated and condensed atoms. This phenomenon usually occurs near resonances and thresholds of the photoabsorption processes where the real and imaginary parts of polarizability are largely different and the real part usually has peaks in these energy regions. While in other regions this characteristic is usually absent. At energies near absorption edges or resonances, the photoabsorption cross section is found to depend on the chemical environment of the atom. However, quantitative analysis of these local structures is not fully developed and remains a challenge. The contributions of the real part of polarizabilities to photoabsorption cross sections can be analysed by taking into account polarization-type many-body effects. This effect, which is essentially a screening of the local field due to the Coulomb interactions, mostly affects dipole matrix elements. Some unresolved differences of the photoabsorption cross sections, especially near thresholds and resonances between isolated and condensed atoms, could probably be interpreted by competition between the imaginary and real parts of atomic frequency-dependent polarizabilities.

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