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Density-dependent photoabsorption cross sections of atomic Xe*

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The evolution of the photoabsorption cross sections of atomic xenon with number densities varying from ideal gas to condensed matter has been studied by an alternative view in the present work. The alternative expressions of the photoabsorption cross sections presented by Sun *et al* recently were used with the local field models that has proven to be generalized easily to multiatomic systems including molecules and condensed phase systems. The present results show that the variation of the photoabsorption cross sections of atomic xenon in the giant resonance region from the isolated to the condensed conditions is very small, which agrees well with the variation law of the solid and gas experiments.

Keywords: condensed-phase photoabsorption, local field, xenon
PACC: 3280F, 3280, 3380E

1. Introduction

The condensed-phase photoabsorption of atoms and molecules embedded such as in liquid, solid and clusters, even under high temperature, high pressure conditions, has always been the problem urgent to be solved in atomic and molecular physics.[1−3] In such high-density multiatomic systems, the shape and intensity of the photoabsorption cross sections would be affected more or less by some local field effects and interatomic interactions, such as electron overlap effects, the dipole-induced dipole interactions etc. The evaluation and explanation of the influence of the interatomic interactions on the photoabsorption cross sections has always been one of the research aims of condensed physics and atomic and molecular physics.[4] The problem of how these interatomic interactions will influence the photoabsorption cross sections has been given more and more attention recently.[5−9] However, to understand the relation between macroscopic electromagnetic responses observed in experiments and microscopic properties such as atomic and molecular polarizabilities still presents a challenge.[10] Usually, the optical response properties of materials are to a large extent governed by the properties of the individual atoms and to some extent by the interactions with the neighbouring atoms.[11] Recently, Sun *et al*[12] and Ma[13] have proposed an alternative method to study the influence of the local field effect on the photoabsorption cross sections of atoms embedded in condensed matter in many models. These alternative expressions of the photoabsorption cross sections were used with the local field models that have proven to be generalized easily to multiatomic systems including molecules and condensed phase systems. The basic idea of these expressions is that the photoionization cross-sections of atoms in a real system can be described as the coupling between quantum quantity (QQ) and classical quantity (CQ) parts clearly. The QQ part represents the photoionization cross sections of an isolated particle, while the CQ part may represent most of the important influence of the macroscopic effects on the photoionization cross-sections. Then, coupling the isolated atomic properties with the environmental effects would open a simple way to understand the response properties of the multiatomic systems. From this very simple view, once the accurate photoabsorption cross sections of the isolated atom have been obtained, the evolution of the photoabsorption cross section from the isolated state to the condensed conditions or multiatomic systems then can be represented by different local field effects directly.

In general, the interactions with the environments will change the atomic properties considerably when compared with the ideal gas ones. The pho-

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toabsorption cross sections of isolated atomic xenon has generated much interest since the discoveries of a broad absorption peak due to the $4d^{10}$ inner-shell cross sections.[14−16] Xenon is a noble gas that has high polarizability which cannot only give rise to substantial interatomic coupling, but also to efficient interactions with optical fields. Isolated xenon atoms have constant isotropic polarizabilities and therefore will not give rise to any Raman response. However, monatomic gases like xenon are known to have a Raman spectrum at higher densities due to a collision-induced anisotropy of the polarizability tensor of pairs of atoms, consisting of nearly symmetric, nearly exponential continua on the Stokes and anti-Stokes sides.[17] This makes atomic liquid such as liquid xenon excellent probes for studies of intermolecular interactions and motions.[18] Liquid xenon was used to investigate the effects of overlapping electron clouds and dipole induced-dipole interactions on the optical response. Xenon is eminently suited for this purpose, since the single atoms do not generate a Raman signal and all observed responses are therefore due to many body effects. Experimentally, photoabsorption cross sections measurements in the ionization continuum regions of xenon have been widely performed using Beer–Lambert law photoabsorption method.[19] These Beer–Lambert photoabsorption experiments could only give accurately the shapes of the photoabsorption cross sections. However, the absolute values of the photoabsorption cross sections in the continuum typically show substantial differences, especially at higher energies, partly due to difficulties in obtaining precise measurements of the sample target density.[20,21] The number density effects on the photoabsorption cross sections are also important in condensed-phase photoabsorption processes. In the present work, the interatomic interactions and the number density effects on the photoabsorption cross sections of atomic xenon have been studied in detail by our general expressions.

2. An alternative view of condensed-phase photoabsorption

In order to study the influence of the macroscopic local field effect on the photoabsorption cross sections and avoid large-scale *ab initio* calculations for the entire condensed matter, recently, Sun *et al*[12] and Ma[13] have proposed a set of strict and general expressions for the photoabsorption cross sections of atoms, which can be generalized easily to multiatomic systems including molecules and condensed phase systems. In their view, the photoabsorption cross sections can be expressed, based on experimental Beer–Lambert's law and Maxwell's equations, generally as[13]

$$\sigma(\omega) = \mathrm{DIF} \times \sigma_{\mathrm{i}}(\omega). \tag{1}$$

The influence of the surrounding atomic interactions with the photo-ionized atom in the arbitrary multiatomic systems on the photoabsorption cross sections can be easily investigated using the so-called dielectric influence function (DIF)[13]

$$\mathrm{DIF} = \frac{1}{2\sqrt{2}\pi N\zeta}\sqrt{\sqrt{\epsilon'^2 + \epsilon''^2} - \epsilon'}, \tag{2}$$

which couples the macroscopic effects and the microscopic property such as photoabsorption cross sections of an isolated atom in a uniform expression. Obviously, the DIF is the function of the number density N of condensed matter and the dielectric functions $\epsilon(\omega) = \epsilon'(\omega) + \mathrm{i}\epsilon''(\omega)$. In Eq.(1), the $\sigma(\omega)$ represents the cross section of the atoms embedded in some condensed matter, while $\sigma_{\mathrm{i}}(\omega)$ represents the cross section of the same atoms which are isolated or in ideal gas. The fundamental and famous expression of photoabsorption cross sections[22] for the isolated atom and molecule used in most theoretical studies $\sigma_{\mathrm{i}}(\omega) = \dfrac{4\pi\omega}{c}\zeta$ is usually invalid to describe the photoabsorption processes in condensed system directly, because it does not include any factor of interatomic interactions and gives only the property of an isolated atom or molecule. In Eq.(2), the ζ is the imaginary part of polarizability $\alpha(\omega)(= \eta + \mathrm{i}\zeta)$ of atoms and ω is the photon energy.

The most important innovation of these new expressions is obviously to couple the local field effects with the isolated atomic properties. This is very useful for studying the properties of the large-scale multiatomic systems. Because for bulk material systems, it is still very difficult to perform the complete quantum mechanics *ab initio* calculations nowadays due to the large requirement of the computation resources. In the present view for condensed phase, the property of the isolated atom can be calculated accurately and easily by the quantum mechanics *ab initio* method

or obtained from experiments, while the environmental interactions among atoms or the influence of the interatomic interactions on the photoabsorption cross sections in the condensed matter might be modelled by some local field models with interatomic effects such as electron overlap effects, the dipole–dipole interactions, the multipole interactions etc. Using this general expression of the photoabsorption cross sections, the evolution of the photoabsorption cross sections from the isolated state to the condensed state can be easily investigated. However, there are still two important factors that can influence the accuracy of the theoretical results greatly. One of them is the accuracy of the local field models for the actual multiatomic systems. The more correct the local field model of the condensed matter, the more accurate the photoabsorption cross sections obtained from this expression will be. The other is the influence of the integral instability of the Kramers–Kronig transformation on the photoabsorption cross sections. In order to obtain the photoabsorption cross sections of condensed atoms from the photoabsorption cross sections of the isolated atoms, the real part of the polarizability should be calculated by the Kramers–Kronig transformation of the imaginary part of polarizability. The accuracy of the photoabsorption cross section will be very sensitive to the infinite integral process, sometimes the theoretical results were wrong thoroughly.[7–9] Searching for more correct local field models and more accurate integral method for Kramers–Kronig transformation is the key job to use these alternative expressions.

In addition, the imaginary part of the polarizability can be obtained directly from the experimental photoabsorption cross sections of the ideal gas using $\zeta(\omega) = \dfrac{c}{4\pi\omega}\sigma_{\mathrm{i}}(\omega)$.[22] Then the real part of the atomic polarizability can be calculated by using some Kramers–Kronig transformation codes.

$$\eta(\omega) = \frac{c}{2\pi^2} P \int_0^{\infty} \frac{\sigma_{\mathrm{i}}(\xi)}{\xi^2 - \omega^2} \mathrm{d}\xi. \qquad (3)$$

However, the real parts of the polarizability calculated usually by using the above Kramers–Kronig transformation from the photoabsorption cross sections of the isolated atoms are very sensitive to the implementation method of the infinite integral.[23] In the present work, we compare several numerical integration methods for Kramers–Kronig transformation and use the most accurate code for numerical solution of Kramers–Kronig transform by a Fourier method[24] to perform the calculations.

3. Calculation and discussion

There are many databases on atomic and molecular spectrum and many packages used to calculate the spectrum of the isolated atomic photoabsorption, so one can easily obtain the accurate photoabsorption cross sections of the atoms in ideal gas nowadays. The existence of the photoabsorption cross sections in a sufficiently wide energy region may ensure the accuracy of the infinite integral of the Kramers–Kronig transformation. In order to obtain the accurate and reliable real part of the polarizability by using the Kramers–Kronig transformation, the photoabsorption cross sections of atomic xenon in a wide energy region (29 to 30000 eV) have been used[25] to perform the infinite integral. Except in the lowest and highest energy regions, this integral method can give enough accurate real parts of polarizability in the middle energy region, especially for the giant resonance region between 45 and 195 eV.[24] Figure 1 shows the calculated imaginary and real parts of the polarizability α of the isolated atomic xenon only in the photon energy region of the giant resonance 45–195 eV, since in this region the local field effects would be strong due to the large polarizabilities. The polarizabilities in 29–45 eV and 195–30000 eV regions have also been calculated but not shown in Fig.1. Performance of the Kramers–Kronig transformation on this wide energy region will guarantee that the calculated real part of the polarizability in 45–195 eV region will be reasonably correct. Then, the subsequent procedure of the calculations cannot be influenced strongly by the integral instability of the Kramers–Kronig transformation. Once the

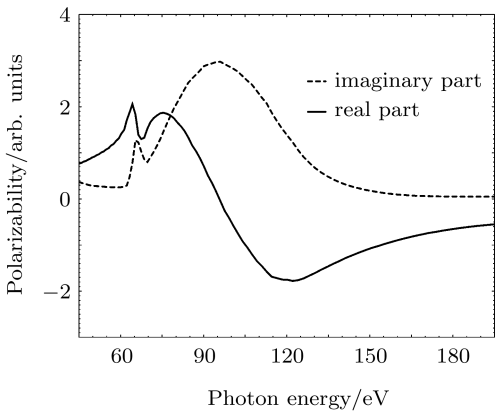


Fig.1. The real and imaginary parts of polarizability of atomic xenon, obtained from the numerical solution of Kramers–Kronig transformation in 29–30000 eV by a Fourier method.

real and imaginary parts of the polarizability have been obtained, the influence of the local field effects on the photoabsorption cross sections of atomic xenon with different number densities can then be studied easily by using different local field models with the present alternative expressions.

In the present work, we study the variations of the photoabsorption cross sections of atomic xenon from the isolated state to the condensed conditions in terms of the famous Clausius–Mossotti (CM) and Onsager models. The dielectric constants ϵ related to the atomic polarizabilities by the Clausius–Mossotti model and Onsager model can be expressed respectively as:

$$\epsilon = 1 + \frac{4\pi N\alpha}{1 - 4\pi N\alpha/3} \tag{4}$$

and

$$\epsilon = 1 + 4\pi N\alpha \frac{3\epsilon}{2\epsilon + 1 - 2\alpha/r^3(\epsilon - 1)}, \tag{5}$$

where the variable r can be taken as the radius of the local cavity. For some simple solids and liquids, these models have been proven very accurate to describe the local fields around the target atoms. In Fig.2, the photoabsorption cross sections of the ideal gas experiment $(\circ\circ\circ)$[25] and the solid phase experiment $(\times\cdots\times)$ or $(\diamondsuit\cdots\diamondsuit)$[19] are compared with the present theoretical results. Because the photoabsorption cross sections of the solid xenon are relative values and calculated using $\sigma = \mu/N$ from solid absorption coefficient μ, the $(\times\cdots\times)$ results have been scaled with the ideal gas experiments $(\circ\circ\circ)$, and the $(\diamondsuit\cdots\diamondsuit)$ results have been also reduced in order to compare easily the shape of peaks in photoabsorption cross sections in the resonant region with the theoretical results. These theoretical results are calculated from the same atomic polarizabilities shown in Fig.1 but in terms of different local field models or number densities. For atomic xenon, the photoabsorption cross sections are almost identical in the ideal gas and solid states because the interactions among atoms in solid are almost the van der Waals interactions.[19] The present theoretical results with the solid number densities in CM $(\cdots)$ model are almost identical with the ideal gas experiments. This shows that the interactions in solid xenon are very weak and almost no influence on the photoabsorption cross sections of the isolated atoms. All of these theoretical photoabsorption cross sections will be convergent to the gas experimental results $(\circ\circ\circ)$ in the ideal gas number density.[12] The ideal gas and the solid state theoretical results are almost identical and in agreement with the experimental results. The most striking difference between the gas and the solid experiments is that there are two peaks in the maximum of solid while there is only one broad peak in gas maximum. The occurrence of these two peaks in solid spectrum may be explained by the interactions between the broad maximum about 90 eV and the sharp maximum about 65 eV of the ideal gas spectrum. When the number density is even larger than solid state, i.e., $N = 0.1a_0^{-3}$ $(---)$ in the CM model, the interactions among dipoles in about 65 and 90 eV regions are very strong. In the CM model the extent of the interactions is only represented by the number densities, so for this very strong interaction the number density is as several hundred times great as the solid number density and obviously unreasonable. In order to reduce the number density, some other variables such as the distance between atoms should be introduced. For example, in the Onsager model, one can use $N = 0.08a_0^{-3}$ and $r = 1.2a_0$ $(— — —)$ to represent this strong interaction. This number density in the Onsager model is more reasonable than that in CM model. The broad maximum at 90 eV has been shifted to the lower energy region and the amplitude has been reduced. The sharp maximum at 65 eV has been increased and the amplitude is almost the same as that of the broad one. In order to compare with the solid experiment, the $(— — —)$ results have been shifted about 30 eV to the higher energy region $(———)$, two peaks have been evolved by our expressions from the ideal gas experimental results which only

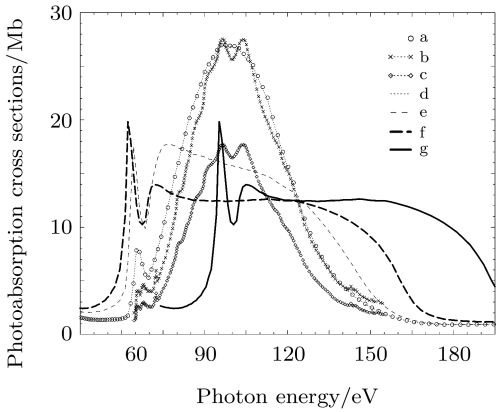


Fig.2. The photoabsorption cross sections obtained in the ideal gas experiment and the solid phase experiment are compared with the present theoretical results. a Expts (gas); b Expts (solid), scaled; c Expts (solid) reduced; d $N = 2.455 \times 10^{-3}a_0^{-3}$, CM model; e $N = 0.1a_0^{-3}$, CM model; f $N = 0.08a_0^{-3}$ with $r = 1.2a_0$, Onsager model; g $N = 0.08a_0^{-3}$ with $r = 1.2a_0$, Onsager model, shifted.

have one peak. However, the difference between the theoretical results and that of the solid experiment is still large. This indicates that the interactions in the cavity cannot represent all of the interactions acting on the photoabsorption atoms, and more local field effects should be considered.

Figures 3 and 4 show the present theoretical photoabsorption cross sections in the photon energy region of 45–195 eV in the CM and Onsager models respectively with the number densities varying from $1.0 \times 10^{-6} a_0^{-3}$ (ideal gas condition) to $1.0 \times 10^{-1} a_0^{-3}$ (even larger than the number density of the solid xenon). The evolution of the photoabsorption cross sections with the number density in the two different models is almost equivalent. With the same number density, the influence of the Onsager model on the photoabsorption cross sections is stronger than CM model. Below the solid number density, there is almost not any variation of the photoabsorption cross section as the number density increases. As the number density increases to a higher density, the first peak begins to increase dramatically while the second broad peak begins to decrease and shift to the lower energy region, and the width of the resonance becomes more and more broad. This disagrees with the actual phenomena in condensed matter that both the dynamics of liquid and the interatomic interactions will make line broaden and spectral shift of the optical spectra of atoms in condensed states. But if one takes the lowest peak of the second maximum in theoretical results as the second peak, then our results agree with the solid experiments well.

In Fig.5, we present the results of the photoabsorption cross section varying with the radius of the cavity or the distance between atoms from $0.1a_0$ to $10a_0$ at the number density of solid $N = 2.455 \times 10^{-3} a_0^{-3}$ using the Onsager model. The size of the radius of the cavity actually represents in general the magnitude of the interactions between atoms in condensed matter. The theoretical study shows that with the increase of radius, these interactions have almost no effect on the photoabsorption cross sections of the ideal gas, and the photoabsorption cross section almost does not vary with the variation of the cavity radius any more. This is because for these distances between atoms, the interactions are very weak and almost no local field effects on the photoabsorption cross sections. When the radius of the cavity is small, for example, about $2a_0$, the photoabsorption cross section decreases very dramatically as the radius decreases. The variation of the photoabsorption cross section with the radius is the same as the variation of the photoabsorption cross section with the number density. As the radius decreases, the interaction among atoms becomes stronger and stronger, and the photoabsorption cross sections in the threshold energy region agree better with those obtained in solid experiment.

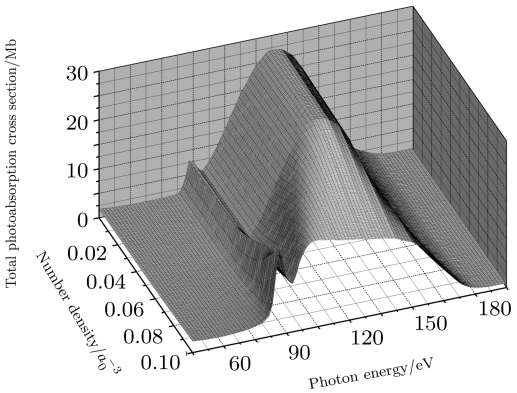


Fig.3. The evolution of the energy-dependent photoabsorption cross sections of atomic xenon with the number density in terms of the Clausius–Mossotti model.

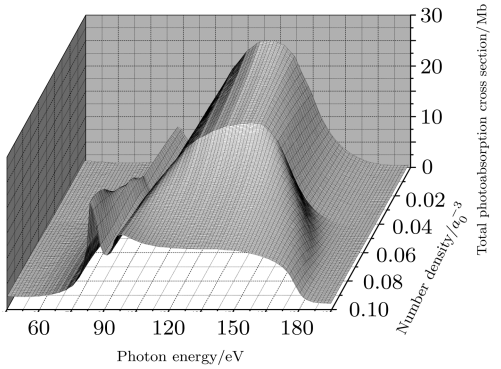


Fig.4. The evolution of the energy-dependent photoabsorption cross sections of atomic xenon with the number density in the Onsager model with $r = 1.2a_0$.

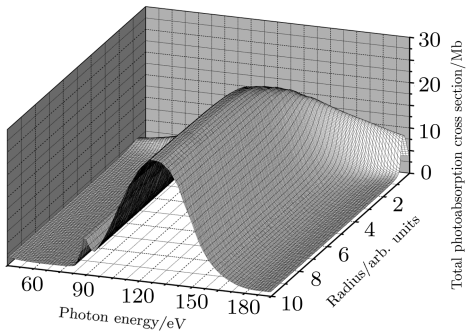


Fig.5. The evolution of the energy-dependent photoabsorption cross sections of atomic xenon with the radius of the cavity in the Onsager model with $N = 2.455 \times 10^{-3} a_0^{-3}$.

4. Conclusion

In the present work, the influence of the macroscopic local field effects on the photoabsorption cross sections of atomic xenon embedded in condensed matter has been studied by using some famous models. All of these models can be applied to the calculation of the photoabsorption cross sections of atoms under the ideal gas condition. This is because the expression for the photoabsorption cross sections of atoms in medium will turn to the expression of isolated atoms. When the number density is greater than that of the ideal gas, the variation of the photoabsorption cross sections of atomic xenon with number density is almost identical for different local field models. In order to describe the average interactions accurately, the results show that it is not enough to take into account only the macroscopic local field effects. To improve the accuracy of the theoretical photoabsorption cross sections of a solid system, other physical effects such as the electron overlap effects should be implemented in the local field models. These interatomic effects could be implemented easily in our alternative expressions of the photoabsorption cross sections.

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