

Optical absorption of angulon in metal halide perovskites

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ABSTRACT

We theoretically study the optical absorption of an angulon in the metal halide perovskites (MHP) based on the improved Devreese–Huybrechts–Lemmens model, where the formation of quasiparticle angulon states originates from the organic cation rotating in the inorganic octahedral cage of MHP. We find that the resonance optical absorption peaks appear when the energy of the incident photon matches the quantum levels of angulon. Moreover, the intensity of absorption depends on the quantum states of phonon angular momentum. These theoretical results provide significant insight to study the redistribution of angular momenta for the rotating molecules immersed in the many-body environment.

1. Introduction

Angulon describing the entity of a rotating particle (molecule or impurity) dressed by the phononic bath around it, has been proposed by Schmidt and Lemeshko for the first time in 2015 [1]. With the help of this quasiparticle concept, the intractable angular momentum algebra for the rotating molecules (or impurities) immersed in a many-body environment is tremendously simplified [2–13]. They predicted a series of novel properties, such as the rotational fine structure of angulon [1,2,10], the angular self-localization effect [7,8,10] and the possible realization of magnetic monopoles [4,11], for molecules rotating in the systems of superfluid helium nanodroplets and Bose–Einstein Condensates [5,6,12]. Some of these properties have been proved by the subsequent experiments [5,14–17]. More importantly, this quasiparticle model can be expanded to study the general systems consisting of molecules rotating in the many-body bath and open up a new door to explore the angular momentum exchange between the rotating particles and its surrounding environment [12].

Metal halide perovskites (MHP) with the general formula of ABX_3 , (A, B and X represent the monovalent organic or inorganic cation, the divalent Pb^{2+} cation and the halide anion, respectively) have aroused extensively interesting owing to their potential applications in optoelectronic and photovoltaic devices [18,19]. One of their unique features is A cation rotating in the BX_6^{4-} cage as shown in Fig. 1, which plays a vital role in modifying the fundamental properties of MHP [20–22]. Some recent experiments have proved that the reorientation of A cation could be thermally activated at certain temperature with the residence time varying from femtoseconds to picoseconds [22,23]. Moreover, its

coupling with the surrounding inorganic framework may give rise to crystal phase transitions between the orthorhombic, tetragonal, and cubic phases with temperature [24,25]. Zhu et al. also certified that the reorientational motion of dipolar A cations could be thermally activated and their coupling with BX_6^{4-} octahedral cage may affect the dynamics of charge carriers [26]. In particular, the ultrafast rotational motion of the A cation in response to the photo-generation of charge carriers induces the formation of large polarons [27,28], which results in an effective screening of the Coulomb potential to hinder hot-carrier scattering. Although the rotational motion of the A cation in MHP has been extensively investigated, studies regarding the angular momentum exchange of the rotational A cation with the BX_6^{4-} octahedral cage and photon, to our best knowledge, are still lacking until now.

In the present paper, we employ MHP as a new platform to explore the angulon. We focus on the optical absorption process of an angulon schemed in Fig. 1, in which an angulon is formed from a $CH_3NH_3^+$ cation rotating in the BX_6^{4-} octahedral cage. The resonance optical absorption coefficients are obtained based on the improved Devreese–Huybrechts–Lemmens (DHL) model that used to study the optical absorption of the traditional polaron extensively in the past decades [29–32]. We compare the intensities of the optical absorption of angulon for different phonon angular momentum quantum states. These theoretical results not only enrich the knowledge of the rotating molecules immersed in the many-body systems, but also provide a simple and direct method to identify the angulon quasiparticle and phonon angular momenta around it.

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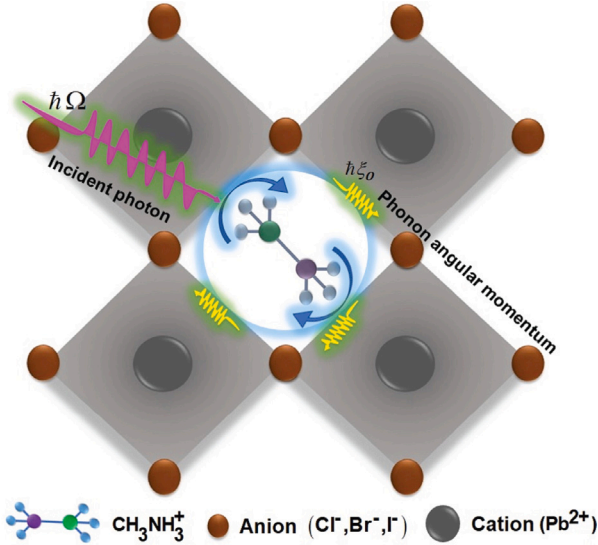


Fig. 1. Schematic diagrams of an angulon and its optical absorption process, in which an angulon is formed arising from a CH_3NH_3^+ cation rotating in the BX_6^{4-} octahedral cage. The resonance optical absorption will be occurred when the incident photon momentum is just equal to the eigenenergy of angulon consisting of the rotating CH_3NH_3^+ cation dressed by phonon angular momenta.

2. Theoretical model

In the frame of the angulon model, the total Hamiltonian for a three-dimensional rotating cation coupling with phonon bath in the octahedral cage, can be written as [1,2,5,10]:

$$\hat{H} = \hat{H}_R + \hat{H}_{ph} + \hat{H}_{R-ph}, \quad (1)$$

with

$$\hat{H}_R = \hbar\xi_0 \hat{\mathbf{L}}^2,$$

$$\hat{H}_{ph} = \sum_{k\lambda\mu} \hbar\omega_v \hat{a}_{k\lambda\mu}^\dagger \hat{a}_{k\lambda\mu},$$

$$\hat{H}_{R-ph} = \sum_{k\lambda\mu} U_\lambda(k) \left[\hat{Y}_{\lambda\mu}^*(\hat{\theta}, \hat{\phi}) \hat{a}_{k\lambda\mu}^\dagger + \hat{Y}_{\lambda\mu}(\hat{\theta}, \hat{\phi}) \hat{a}_{k\lambda\mu} \right],$$

where the first term $\hat{H}_R$ describes the kinetic energy for the rotational motion of the linear molecule with the rotational constant ξ_0 , $\hat{\mathbf{L}}$ is the angular momentum operator. The three-dimensional rotational eigenstates $|l, m\rangle$ are labeled by the orbital angular quantum number l and its projection m on the laboratory z axis, with eigenenergies $E_l = \hbar\xi_0 l(l+1)$. The second term H_{ph} stands for the kinetic energy of the phonons with the dispersion relation $\omega_v = ck$ (here, the acoustic phonon mode is mainly considered and c is the velocity of phonon mode). $\hat{a}_{k\lambda\mu}$ and $\hat{a}_{k\lambda\mu}^\dagger$ are the annihilation and creation operators for the phonon with the wave vector k , which are expressed in the angular momentum representation with λ and μ define, respectively, the phonon angular momentum and its projection on the laboratory-frame z axis; see Refs. 1, 2 and 9 for details. $\hat{H}_{R-ph}$ is the interaction term between the rotating molecular cation and the phononic bath with the angular-momentum dependent strength [1,2]

$$U_\lambda(k) = u_\lambda \sqrt{\frac{8\beta k^{3/2}}{2\lambda+1}} \int f_\lambda(r) j_\lambda(kr) r^2 dr, \quad (2)$$

where u_λ and $f_\lambda(r)$ define the strength and the interaction potential function in the angular momentum channel λ , respectively. The parameter $\beta = \sqrt{D^2/(\hbar\rho c^3)}$ describes the acoustic phonon modes stemming from the deformation potential mechanism [33–35], which depends on

the deformation potential constant D , density ρ and propagating velocity of phonon modes. $\hat{Y}_{\lambda\mu}(\hat{\theta}, \hat{\phi})$ are the spherical harmonics, depending on the angle operators $\hat{\theta}$ and $\hat{\phi}$. $j_\lambda(kr)$ is the spherical Bessel function of the first kind and the summation of wave vector satisfies the relation of $\sum_k \equiv \int dk$, the detailed processes have been given in Refs. 1 and 2. The octahedral cage of MHP shown in Fig. 1 is approximated by the spherical cage with the effective radius $\mathfrak{R}$, so the interaction potential function $f_\lambda(r)$ is assumed satisfying the following form

$$f_\lambda(r) = \begin{cases} \left(\frac{r}{\mathfrak{R}}\right)^\lambda, & (r \leq \mathfrak{R}) \\ 0, & (r > \mathfrak{R}) \end{cases}, \quad (3)$$

which can be attributed to the fact that the organic cation rotating freely in the octahedral cage in pseudo-cubic and cubic phase proved by recent experiments [22–24]. In principle, this potential distribution function could be applied to molecules or impurities rotating in other cage-like structures, such as carbon nanotubes [36] and fullerenes [37].

In usual, many-body systems describing by Eq. (1) are very difficult to solve. Analogue to the polaron theory, Schmidt and Lemesko introduced two canonical transformations to study this problem for the first time [2]. The first canonical transformation allows to transfer the many-body environment degree of freedom into the frame corotating along with the organic cation, which is given by

$$\hat{S}_1 = e^{-i\hat{\phi}} \otimes \hat{\Lambda}_z e^{-i\hat{\theta}} \otimes \hat{\Lambda}_y e^{-i\hat{\gamma}} \otimes \hat{\Lambda}_z, \quad (4)$$

where $\hat{\phi}$, $\hat{\theta}$, and $\hat{\gamma}$ are the angular operators of the rotational cation in the Hilbert space and $\hat{\Lambda} = \sum_{k\lambda\mu\nu} \hat{a}_{k\lambda\mu}^\dagger \sigma_{\mu\nu}^\lambda \hat{a}_{k\lambda\nu}$ is the collective angular-momentum operator of the many-body phononic bath in Hilbert space with σ^λ stands for the vector of matrices fulfilling the angular-momentum algebra in the angular momentum state λ . After performing the first transformation, the Hamiltonian of Eq. (1) is converted into [1,2]

$$\begin{aligned} \hat{\mathcal{H}} = \hat{S}_1^{-1} \hat{H} \hat{S}_1 = & \hbar\xi_0 (\hat{\mathbf{L}}' - \hat{\Lambda})^2 + \sum_{k\lambda\mu} \hbar\omega_v \hat{a}_{k\lambda\mu}^\dagger \hat{a}_{k\lambda\mu} \\ & + \sum_{k\lambda} V_\lambda(k) [\hat{a}_{k\lambda 0}^\dagger + \hat{a}_{k\lambda 0}], \end{aligned} \quad (5)$$

with $V_\lambda(k) = U_\lambda(k) \sqrt{(2\lambda+1)/(4\pi)}$ and $\hat{\mathbf{L}}'$ is an anomalous angular momentum operator, because the components of $\hat{\mathbf{L}}'$ follows anomalous commutation relations in the body fixed frame, differing from the normal operator $\hat{\mathbf{L}}$ of Eq. (1) in the laboratory frame, the detailed derivations have been given in Ref. [9].

The transformed Hamiltonian is further simplified by introducing the second canonical transformation

$$\hat{S}_2 = \exp \left[\sum_{k\lambda} F_{k\lambda}^* \hat{a}_{k\lambda 0}^\dagger - F_{k\lambda} \hat{a}_{k\lambda 0} \right], \quad (6)$$

where $F_{k\lambda}$ ($F_{k\lambda}^*$) is the variational function. The details of the derivation processes for the second canonical transformation and the variational function are presented in the supplemental materials. Then, the Hamiltonian is approximated by

$$\begin{aligned} \tilde{H} = \hat{S}_2^{-1} \hat{\mathcal{H}} \hat{S}_2 \approx & \tilde{H}_0 \\ = & \hbar\xi_0 \hat{\mathbf{L}}'^2 + \sum_{k\lambda} [\hbar\omega_v - \hbar\xi_0 (\sum_i \sigma_{0i}^\lambda \sigma_{i0}^\lambda)] \\ & \times (\hat{a}_{k\lambda 0}^\dagger + F_{k\lambda}) (\hat{a}_{k\lambda 0} + F_{k\lambda}^*) - \hbar\xi_0 (\hat{\mathbf{L}}' \cdot \hat{\Lambda} + \hat{\Lambda} \cdot \hat{\mathbf{L}}') \\ & + \sum_{k\lambda} [V_\lambda(k) (\hat{a}_{k\lambda 0}^\dagger + F_{k\lambda}) + V_\lambda(k) (\hat{a}_{k\lambda 0} + F_{k\lambda}^*)] \\ & + \hbar\xi_0 \sum_{k\lambda} (\hat{\Lambda}^2 + \sum_i \sigma_{0i}^\lambda \sigma_{i0}^\lambda \hat{a}_{k\lambda 0}^\dagger \hat{a}_{k\lambda 0}) \\ & + \sum_{k\lambda\mu} \hbar\omega_v \hat{a}_{k\lambda\mu}^\dagger \hat{a}_{k\lambda\mu} - \sum_{k\lambda} \hbar\omega_v \hat{a}_{k\lambda 0}^\dagger \hat{a}_{k\lambda 0}, \end{aligned} \quad (7)$$

with $i = \pm 1$. These terms of mainly contribution in $\tilde{H}_0$ have been reserved. The eigenfunction of angulon can be choose as $|\Phi\rangle = |lm\rangle |0_{ph}\rangle$, where $|0_{ph}\rangle$ denotes the vacuum state of phonon, satisfying the relation

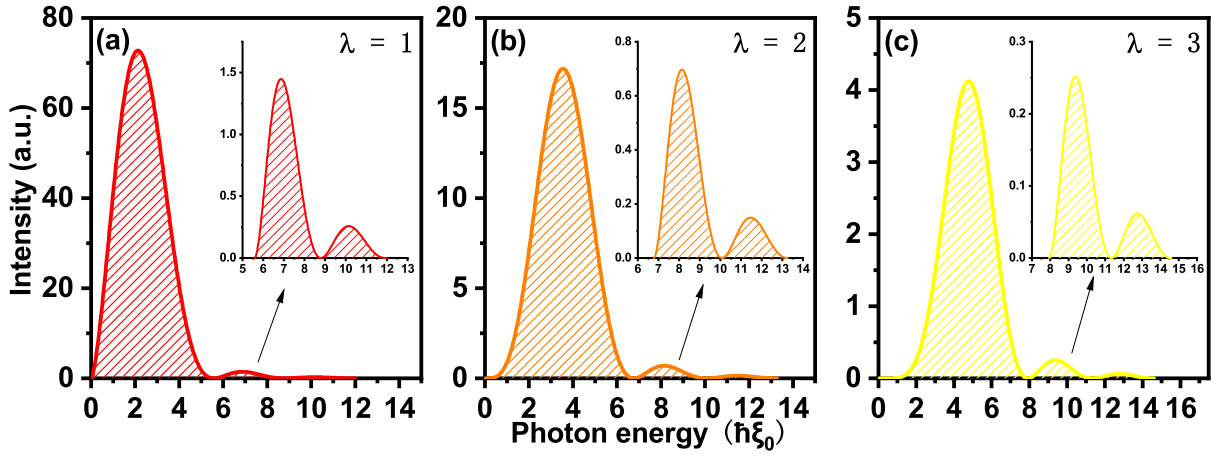


Fig. 2. The optical absorption of an angulon as a function of the photon energy for different quantum states of phonon angular momentum $\lambda = 1$ (a), $\lambda = 2$ (b) and $\lambda = 3$ (c). The incident photon energy is in units of $\hbar\xi_0$.

of $\hat{a}_{k\lambda 0}|0_{ph}\rangle = 0$. The optical absorption will be calculated here for the total momentum of the system $l' = 0$. Thus, the expectation values of the eigenenergies of angulon can be obtained via

$$E = \sum_{k\lambda} [\hbar\omega_v + \hbar\xi_0\lambda(\lambda+1)] F_{k\lambda} F_{k\lambda}^* + \sum_{k\lambda} V_\lambda(k) (F_{k\lambda} + F_{k\lambda}^*), \quad (8)$$

Minimizing Eq. (8) with respect to $F_{k\lambda}^*$ and $F_{k\lambda}$ (see supplemental materials), one can get

$$F_{k\lambda}^* = F_{k\lambda} = -\frac{V_\lambda(k)}{\hbar\omega_v + \hbar\xi_0\lambda(\lambda+1)}. \quad (9)$$

Substituting Eq. (9) into Eq. (8), the energy of angulon could be expressed as

$$E = -\sum_{k\lambda} \frac{|V_\lambda(k)|^2}{\hbar\omega_v + \hbar\xi_0\lambda(\lambda+1)}. \quad (10)$$

Based on the Fermi's golden rule, the absorption coefficient $\Gamma(\hbar\Omega)$ for an incident photon with energy $\hbar\Omega$ from the ground state of an angulon is [29–31]

$$\begin{aligned} \Gamma(\hbar\Omega) &= \sum_f |\langle\Phi_0|\boldsymbol{\zeta} \cdot \mathbf{B}|\Phi_f\rangle|^2 \delta(E_0 + \hbar\Omega - E_f) \\ &= \frac{2\pi\hbar\eta}{\epsilon_v B^2} \sum_f |\langle\Phi_0|M|\Phi_f\rangle|^2 \delta(E_0 + \hbar\Omega - E_f), \end{aligned} \quad (11)$$

where $\boldsymbol{\zeta}$ is the magnetic moment of rotating organic cation and $\mathbf{B}$ is the magnetic field vector of the incident photon; η and ϵ_v are the permeability and permittivity of the medium, respectively. $M = \gamma_0 \mathbf{L} \cdot \mathbf{B}$ is the time dependent perturbation term ($\gamma_0 = e/2m_0c_0$), describing the orbital magnetic momentum $\gamma_0 \mathbf{L}$ of the rotational organic cation interacts with the magnetic vector of the incident photon. Φ_0 denotes the ground state of an angulon with the eigenenergy E_0 . The possible final state is described by Φ_f with the eigenenergy E_f . In fact, the final state includes all possible excited states of the angulon that are so poorly known. Namely, the calculations of absorption coefficient are very difficult in practice.

Several decades ago, Devreese et al. [29] proposed a very simple model to explore the optical absorption of polaron in traditional semiconductors, in which all the excited states of polaron were simplified via two unitary transformations, thus to avoid the requirement of accurate description for these final polaron states. Getting an enlightenment from this pioneering work, we expand this model to the optical

absorption of angulon. After the rigorous derivation presented in the supplemental materials, the absorption coefficient can be expressed as

$$\begin{aligned} \Gamma(\hbar\Omega) &= \frac{\pi\hbar\eta\gamma_0^2}{3\epsilon_v} \sum_{k\lambda} \hbar\xi_0\lambda(\lambda+1) |F_{k\lambda}|^2 \\ &\times \delta[\hbar\Omega - \hbar\omega_v - \hbar\xi_0\lambda(\lambda+1)]. \end{aligned} \quad (12)$$

Substituting Eq. (9) into Eq. (12) and using the properties of δ -function, Eq. (12) becomes

$$\begin{aligned} \Gamma(\hbar\Omega) &= \frac{4\pi\eta\gamma_0^2 c^{3/2} \xi_0 \beta}{3\Re^3 \epsilon_v} \\ &\times \frac{u_\lambda^2 \lambda(\lambda+1) J_{\lambda+3/2}^2 [\Re(\Omega - \xi_0\lambda(\lambda+1))/c]}{(\Omega)^2 [\Omega - \xi_0\lambda(\lambda+1)]^{3/2}}, \end{aligned} \quad (13)$$

where $J_{\lambda+3/2}$ is the Bessel function of the first kind for the quantum state of phonon angular momentum λ .

In the numerical simulation, the typical example of MHP $\text{CH}_3\text{NH}_3\text{PbI}_3$ in cubic phase is selected, in which organic cation CH_3NH_3^+ rotating in the PbI_6^{4-} octahedral cage as schemed in Fig. 1. The values for related parameters are listed below. The conditions $1.75u_1 = 3.06u_2 = 5.36u_3 = u_0$ for the strength parameters for three lowest angular momentum channels are assumed [1,2]. The effective radius $\Re = 3.63 \text{ \AA}$ and the velocity of acoustic phonon modes $c = 2200 \text{ m/s}$ are selected [20,21]. Taking these parameters into Eq. (13), the optical absorption of an angulon are shown in following figures.

3. Results and discussion

Fig. 2 shows the optical absorption of an angulon as a function of the incident photon energy ($\hbar\Omega$) for three different quantum states of phonon angular momentum $\lambda = 1, 2, 3$. For $\lambda = 1$ in Fig. 2(a), one can see that the resonance absorption peaks with different densities will be appeared as the energy of incident photon matching the total energies of the phonon and its rotational motion. The similar behaviors are also obtained for $\lambda = 2$ and $\lambda = 3$ in Fig. 2(b) and (c), respectively. Obviously, these resonance peaks imply a series of eigenstates of angulon, representing the total angular momentum quantum states of the phonon bath corotating with the organic cation, which suggest that different angulon states could be directly reflected by the absorption spectroscopy. Initially, Schmidt and Lemesko proposed that the angulon induces a rich rotational fine structure [1,2], for instance, the rotational Lamb shifts that are very consistent with the previous observations in spectra of the rotating molecules embedded

in superfluid helium nanodroplets [38–40] and the appearance of two angulon branches due to the isotropic effect of the finite-range potential between rotating particle and phonon bath. Soon afterwards, they proposed that the angulon spectral function for different orbital quantum states shows a discontinuity with the rotational velocity of the quantum impurity, implying the behavior of the transfer of one quanta of angular momentum from the phonon bath to the rotating impurity at a particular rotational velocity [2,8,9]. This behavior may be explained by the resonance absorption peak shown in Fig. 2. But only one discontinuous point is obtained in their model for the certain orbital angular momentum state. Here, we predict that there should, in fact, exist other discontinuous points denoting the angular momentum transfer with increasing the rotational velocity in Ref. [2], just like multiple resonance peaks as given in Fig. 2. Though the dispersion relation and interaction form must affect the basic properties of angulon quasi-particle a lot which are different in superfluid and perovskites, the core is to verify the formation of angulon or the transfer of angular momenta of phonons in different platforms. Furthermore, they studied the variation of the deformation of phonon density (or the average number of phonon angular momentum) around the unstable angulon state and pointed out the variational shape of phonon density could serve as a fingerprint of the angular-momentum exchange [2, 8,9]. The microscopic theory of Raman scattering predicted that the Raman spectra provide an effective and direct method to reflect the transfer of phonon angular momentum and its specific values in many-body environment [41]. Yakaboylu et al. found that angulon could induce anomalous screening even in a neutral and weakly polarizable environment and suggested that this angulon can be evaluated just by a single angular-momentum-dependent screening factor related to several observables, such as the effective Rabi frequency, geometric phase and molecular spatial alignment [3]. In addition, Lemeshko also proposed that the angulon effect could be seen indirectly from renormalization of the effective molecular moments of inertia, which is in good agreement with experimental measurements for a broad range of molecular impurities species [5]. Although so many strategies above mentioned have been proposed for identifying the angulon effect, the optical absorption provides a more direct and effective way to study this problem.

We only discuss one type of rotational motion of the organic cation in the octahedral cage in this paper. Indeed, there are several different types of rotation motions with different rotational inertias in this structure, both of which could be reflected in the resonance absorption with the distinctly rotational constant as shown in Fig. 2. Hence, this model lays the theoretical foundation to analyze the rotational dynamics of the molecule immersed in the quantum many-body environment by absorption spectroscopy. Usually, MHP materials undergo two structural phase transitions with temperature, such as the crystal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ changes from orthorhombic to tetragonal at about temperature $T = 160$ K and then to the cubic phase at about $T = 330$ K [22,42]. These phase transitions not only have a significant influence on the strength of the electron–phonon interaction and phonon energy, but also modify the distribution of the interaction potential between the rotating cation and the phonon bath. Consequently, different types of rotational motion of cation possessing different the molecular moments of inertia could be reflected directly by the different resonance absorption peaks of angulon. Therefore, the optical absorption of angulon may provide a valuable and direct resolution method to study the phase transitions in the MHP materials. We hope that these theoretical results can stimulate the progress of the related experiments. Finally, we must emphasize that (1) the ferroelectric and anti-ferroelectric properties in $\text{CH}_3\text{NH}_3\text{PbI}_3$ remains controversial [43–45], so we do not consider specific space groups here; (2) at room temperature, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals exhibit pseudo-cubic lattice cages, but the cations are not restricted to two-dimensional rotation similar to the mode in tetragonal phase [20,46]. Thus, our model can be used for the cation rotating in organic–inorganic hybrid perovskite-based devices operating at room temperature.

4. Conclusion

In summary, the optical absorption of an angulon is studied in MHP based on an improved Devreese–Huybrechts–Lemmens model proposed in traditional semiconductors for polarons. We find that multiple resonance absorption peaks are appeared as the incident photon matches the total energies of acoustic phonon and its rotational motion, where the intensities of optical absorption decrease with quantum states of phonon angular momentum. These theoretical results indicate that (i) optical absorption could be served as an effective and simple method to identify the angulon quasiparticle; (ii) the organic cation rotating in the lattice cage in MHP provides a new platform to study the redistribution of orbital angular momentum in quantum many-body systems.

See the supplementary material for the details about the derivation for the variational function and the derivation for the optical absorption coefficient of an angulon.

CRediT authorship contribution statement

Jia-Wei Wu: Methodology, Data curation. **Yu Cui:** Investigation, Formal analysis, Methodology, Writing. **Shao-Juan Li:** Resources, Visualization. **Zi-Wu Wang:** Writing, Validation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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The data that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.physb.2023.415335>.

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