

Ultrafast spontaneous exciton dissociation via phonon emission in BiVO₄Stephen E. Gant^{1,2}, Antonios M. Alvertis³, Christopher J. N. Coveney⁴, Jonah B. Haber⁵, Marina R. Filip⁴, and Jeffrey B. Neaton^{1,2,6}¹Department of Physics, University of California Berkeley, Berkeley, California 94720, USA²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA³KBR, Inc., NASA Ames Research Center, Moffett Field, California 94035, USA⁴Department of Physics, University of Oxford, Oxford OX1 3PJ, United Kingdom⁵Materials Science and Engineering, Stanford University, Stanford, California 94305, USA⁶Kavli Energy NanoScience Institute at Berkeley, Berkeley, California 94720, USA

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Monoclinic bismuth vanadate (m-BiVO₄) is a promising indirect band gap semiconductor for photoelectrochemical water splitting, yet the characteristics of its low-lying photoexcitations, or excitons, remain poorly understood. Here, we use an *ab initio* Bethe-Salpeter equation approach that incorporates phonon screening to compute the nature and lifetimes of the low-lying excitons of m-BiVO₄. Our calculations indicate that at 0 K, the lowest-lying exciton energy exceeds the indirect band gap, enabling spontaneous dissociation into free carriers via phonon emission within picoseconds. At 300 K, both phonon emission and absorption effects reduce this timescale to only a few femtoseconds. Phonon screening also greatly reduces the binding energy of the lowest-lying exciton, leading to an optical absorption spectrum that better reproduces experimental measurements. Overall, our findings establish the general conditions under which phonon emission-driven exciton dissociation can occur in indirect gap semiconductors, and they emphasize the critical role phonon screening can play in predictive calculations of photophysical properties of complex materials.

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I. INTRODUCTION

Monoclinic bismuth vanadate (m-BiVO₄) is a prominent candidate photocatalyst for solar water splitting applications due to its visible-range light absorption, favorable band edge energies versus water reduction and oxidation potentials, and its stability under operating conditions [1–8]. Notably, m-BiVO₄-based devices have achieved some of the highest measured solar-to-hydrogen conversion efficiencies [9,10]. A wealth of calculations have been performed to understand the electronic structure and optical properties of m-BiVO₄. These theoretical investigations have computed its band structure [11–16], its optical absorption spectrum [12,16–19], its defects [20–23] and polarons [24–30], the magnitude of phonon contributions to electronic states [16], and its properties at surfaces and interfaces [18,31–34].

Nonetheless, the nature of the photoexcitations, or excitons, of m-BiVO₄ and their dissociation into free carriers—an important energy transduction step [2,6,35,36]—remains less well understood. In particular, prior calculations that neglect the effects of lattice vibrations, or phonons, predict a strong in-gap excitonic peak [16–19] that is inconsistent with measured

absorption spectra at room temperature [37]; these calculations also predict a relatively large exciton binding energy of ~0.1 eV [16,19], a value that in principle could hinder the rapid dissociation of excitons into free carriers. However, the large reported effects of electron-phonon coupling on the band gap of m-BiVO₄ [16], as well as its large static dielectric constant [38–40], suggest that phonons may play a critical role in screening excitons.

In this article, we compute the properties of low-lying excitons in m-BiVO₄ at finite temperatures using a state-of-the-art *ab initio* Bethe-Salpeter equation (BSE) approach that includes dynamical screening due to phonons at lowest order in the electron-phonon interaction [41–44]. We find that phonon screening significantly reduces the predicted binding energies of the lowest-lying zero center-of-mass momentum exciton compared to the clamped-ion limit. Furthermore, our calculations predict a large linewidth at room temperature associated with the ultrafast dissociation of this exciton into free electron and hole carriers via phonon emission and absorption. We demonstrate that the indirect band gap of m-BiVO₄ enables exciton dissociation via phonon emission—a spontaneous process that can occur even at zero temperature. Finally, our calculations incorporating phonon effects bring the room-temperature linear absorption spectrum into better agreement with experimental measurements [37]. Our findings reveal that phonon emission-driven exciton dissociation can enable the rapid photogeneration of free carriers even at low temperatures, with broad implications for other indirect band gap semiconductors exhibiting strong electron-phonon coupling.

II. METHODS

A. Theory

In the standard *ab initio* *GW*-BSE approach [45–50], the BSE can be written in reciprocal space within the Tamm-Dancoff approximation [50] as

$$\Delta_{\text{cv}\mathbf{k}} A_{\text{cv}\mathbf{k}}^S + \sum_{\text{c}'\mathbf{v}'\mathbf{k}'} K_{\text{cv}\mathbf{k},\text{c}'\mathbf{v}'\mathbf{k}'}(\Omega) A_{\text{c}'\mathbf{v}'\mathbf{k}'}^S = \Omega^S A_{\text{cv}\mathbf{k}}^S, \quad (1)$$

where $\Delta_{\text{cv}\mathbf{k}} = E_{\text{c}\mathbf{k}} - E_{\text{v}\mathbf{k}}$ are the single-particle energy differences (usually computed in the *GW* approximation [45,51,52]) between occupied (v) and unoccupied (c) states at the reciprocal lattice points $\mathbf{k}$ and $\mathbf{k}'$, respectively. $K_{\text{cv}\mathbf{k},\text{c}'\mathbf{v}'\mathbf{k}'}(\Omega) = \langle \text{cv}\mathbf{k} | K(\Omega) | \text{c}'\mathbf{v}'\mathbf{k}' \rangle$ is the dynamical two-particle interaction kernel in the electron-hole basis, and Ω^S and $A_{\text{cv}\mathbf{k}}^S$ are the eigenvalue and eigenvector solutions with corresponding index S . In Eq. (1), we restrict our focus to zero center-of-mass momentum ($\mathbf{Q} = 0$) excitons, as they are the most relevant photoexcitations for optical absorption. Furthermore, we neglect spin-orbit coupling effects, noting they are minimal at the band edges in m-BiVO₄ (see Sec. S1.1.2 in the Supplemental Material [29,53,54]). For singlets, the interaction kernel K in the standard BSE includes bare exchange K^X and screened direct interaction K^D terms [49,50].

In this work, we include the additional screening term K^{ph} in the BSE kernel; it encodes, to lowest order in the electron-phonon interaction, the phonon-mediated screened interaction W^{ph} between electron-hole pairs [41,42,55,56]. K^{ph} depends on both phonon occupations and temperature, and it can be expressed in the clamped-ion exciton basis ($A_{\text{cv}\mathbf{k}}^S$) for the emission (−) and absorption (+) channels as [42]

$$\begin{aligned} K_{SS'}^{\text{ph}}(\Omega, T) &= \sum_{\substack{\pm \nu \text{cv}\mathbf{k} \\ \text{c}'\mathbf{v}'\mathbf{k}'}} A_{\text{cv}\mathbf{k}}^S {}^* A_{\text{c}'\mathbf{v}'\mathbf{k}'}^{S'} g_{\text{ckc}'\mathbf{k}'\nu} g_{\text{vkv}'\mathbf{k}'\nu}^* \mathcal{N}_B^{\pm} \\ &\times \left[\frac{1}{\Omega - \Delta_{\text{cv}\mathbf{k}} \pm \omega_{\mathbf{k}-\mathbf{k}',\nu} + i\eta} + (\text{cv}\mathbf{k} \leftrightarrow \text{c}'\mathbf{v}'\mathbf{k}') \right]. \end{aligned} \quad (2)$$

In Eq. (2), the second term is the same as the first but with the permutation of the $\text{cv}\mathbf{k}$ indices with their primes. $\omega_{\mathbf{k}-\mathbf{k}',\nu}$ is a phonon frequency for the mode ν and momentum $\mathbf{k} - \mathbf{k}'$, the electron-phonon coupling matrix element associated with this phonon is $g_{\text{nk}\mathbf{m}\mathbf{k}'\nu} = \langle \text{nk} | g_{\mathbf{k}-\mathbf{k}',\nu} | \text{mk}' \rangle$ [57], $\mathcal{N}_B^{\pm} = \pm \frac{1}{2} - \frac{1}{2} - n_B$ is the effective Bose-Einstein occupation factor where n_B is the standard Bose occupation of a phonon of energy ω at temperature T , and η is a small positive number needed for numerical convergence (Secs. S1.4.3 and S2 in the Supplemental Material [42,44,53,57–60]). In Eq. (2), we have omitted the thermal occupation terms of the electron-hole states since, for the temperatures considered in this work, they are much smaller than those of the phonons [42].

Unlike for K^D , dynamical effects for K^{ph} are non-negligible because the energy scales of phonons and exciton binding energies are comparable [41,49,50]; this has two important implications. First, it becomes possible for the imaginary part of K^{ph} to be nonzero, indicating finite exciton lifetimes due to dissociation into free electrons and holes [43]. Second, the real part of K^{ph} can vary significantly with respect

to the exciton energy Ω , and the phonon-screened exciton energy must then be solved for self-consistently.

Except for the evaluation of the optical absorption spectra, we retain only the diagonal components of $K_{SS'}^{\text{ph}}$ when evaluating the change to the exciton energy; this approximation is discussed and justified in Appendix B and Ref. [42]. The self-consistent equation for the exciton energy in the diagonal approximation is then

$$\tilde{\Omega}^S(T) = \Omega_0^S + K_{S,S}^{\text{ph}}(\text{Re}\{\tilde{\Omega}^S\}, T), \quad (3)$$

where Ω_0^S is the clamped-ion exciton energy. Appendix B shows that diagonalizing the BSE with nonzero off-diagonal elements in $K_{SS'}^{\text{ph}}$ for the first 70 lowest energy S states affects results by only a few millielectronvolts.

As discussed in Refs. [42,43], both the real and imaginary parts of $\tilde{\Omega}^S(T)$ have physical significance. The real part corresponds to the exciton energy including phonon screening, while the imaginary part is related to the linewidth γ^S associated with the exciton dissociating into a free electron-hole pair via the emission (−) or absorption (+) of a phonon according to the Fermi's Golden rulelike expression:

$$\begin{aligned} \gamma^S(T) &= 2\pi \sum_{\substack{\pm \nu \text{cv}\mathbf{k} \\ \text{c}'\mathbf{v}'\mathbf{k}'}} A_{\text{cv}\mathbf{k}}^S {}^* A_{\text{c}'\mathbf{v}'\mathbf{k}'}^S g_{\text{ckc}'\mathbf{k}'\nu} g_{\text{vkv}'\mathbf{k}'\nu}^* |\mathcal{N}_B^{\pm}| \\ &\times [\delta(\tilde{\Omega}^S - \Delta_{\text{cv}\mathbf{k}} \pm \omega_{\mathbf{k}-\mathbf{k}',\nu}) + (\text{cv}\mathbf{k} \leftrightarrow \text{c}'\mathbf{v}'\mathbf{k}')]. \end{aligned} \quad (4)$$

The dissociation lifetime is then $\tau^S = (\gamma^S)^{-1}$.

Following Refs. [41–43], Eqs. (2)–(4) neglect electron-phonon self-energy corrections to the single-particle energies (Fan-Migdal and Debye-Waller self-energies [57]). Here, as summarized in Sec. S3.2 in the Supplemental Material [16,53,60,61], we find that dressing the single-particle eigenvalues used in K^{ph} with electron-phonon self-energy corrections does not significantly alter the real part of K^{ph} , and the imaginary part of K^{ph} continues to exhibit ultrafast room-temperature dissociation via phonon emission but at a rate that is $\sim 2\times$ times slower. We also observe that the overall effects of electron-phonon renormalization on the lowest-lying exciton energy are well approximated by incorporation of phonon screening via Eq. (2) and a scissor shift of solutions to Eq. (3) that neglect electron-phonon self-energy corrections to the single-particle energies in its kernel; this approximation is employed in Fig. 4. Further justifying this approach, it is discussed in Refs. [41–43,62–65] and Sec. S3.1 in the Supplemental Material [53] that higher-order electron-phonon effects are expected to cancel the effects of these neglected single-particle corrections on the exciton binding energy.

Both phonon emission- and absorption-driven processes contribute to the imaginary part of K^{ph} , provided that energy and momentum conservation are satisfied. While dissociation via phonon absorption requires a nonzero phonon population that occurs at finite temperatures, dissociation via phonon emission can occur at zero as well as finite temperatures. In direct gap materials, absorption-driven dissociation of an exciton with energy Ω^S is energetically forbidden unless $\omega \geq E_{\text{g}}^{\text{dir}} - \Omega^S$, where $E_{\text{g}}^{\text{dir}}$ is the lowest energy direct single-particle gap and ω is the frequency of a phonon. In indirect gap materials, this constraint is $\omega \geq E_{\text{g}}^{\text{ind}} - \Omega^S$, where $E_{\text{g}}^{\text{ind}}$

is the lowest indirect gap. For phonon emission-driven dissociation in direct gap systems, the condition $E_g^{\text{dir}} \leq \Omega^S$ must hold, typically prohibiting this channel for the lowest bound exciton (but allowing it for resonant excitons). For indirect gap systems, the constraint for dissociation via phonon emission is $E_g^{\text{ind}} \leq \Omega^S$. We refer to Appendix A and Sec. S4 in the Supplemental Material [53] for more details on this.

In m-BiVO₄, the conditions for both emission- and absorption-driven exciton dissociation are met for the lowest-lying exciton after solving Eq. (3). While the constraint for emission-driven exciton dissociation can be satisfied in other indirect gap semiconductors, the density of final free electron and hole states into which an exciton can scatter into is not guaranteed to be large. However, because m-BiVO₄ is an indirect gap semiconductor with relatively flat bands that have lower/higher-energy conduction/valence states to scatter into that are close to the direct gap, a large rate of phonon emission-driven dissociation is possible. Moreover, because this process in indirect gap systems scatters the electron and hole to valence and conduction band extrema away from the lowest direct gap, the associated matrix element of this process can be small because A_{cvk} is peaked around the $\mathbf{k}$ points near the direct gap.

B. Calculation details

To investigate this, we perform *ab initio* BSE calculations with K^{ph} for m-BiVO₄ [66] evaluating temperature-dependent dissociation rates and renormalized exciton binding energies. Our *ab initio* calculation of the BSE with phonon screening begins with density functional theory (DFT) calculations [67–74] using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [75] to generate the Kohn-Sham eigensystem, and we then use density functional perturbation theory (DFPT) to calculate the phonon eigensystem and electron-phonon coupling constants [58,76–81]. These quantities are subsequently used as input to the GW and BSE calculations [19,45,52,82–85] in this work (Sec. S1 in the Supplemental Material [53]).

III. RESULTS

A. Exciton binding energy

The quasiparticle band structures computed with DFT-PBE and G_0W_0 @PBE are shown in Fig. 1 and are consistent with prior work [16,19]. Notably, our G_0W_0 @PBE direct band gap is 3.45 eV, a significant increase over the DFT-PBE result of 2.13 eV but considerably larger than the measured direct gap of 2.7 eV [37]. This difference can be rationalized by a large renormalization of the electronic band structure via electron-phonon interactions [16]. The band gap is indirect, and interestingly, the valence band maximum, conduction band minimum, nor the smallest direct gap are located along the high-symmetry paths shown in Fig. 1(a). Instead, the smallest direct gap lies at a lower symmetry point near Γ and A in the irreducible wedge of Brillouin zone (BZ). Near this point, there are also higher- and lower-energy valence and conduction band states that give a G_0W_0 @PBE indirect band gap of 3.35 eV; Fig. 1(b) contains the path that shows both of these direct and indirect gaps. These values are close to

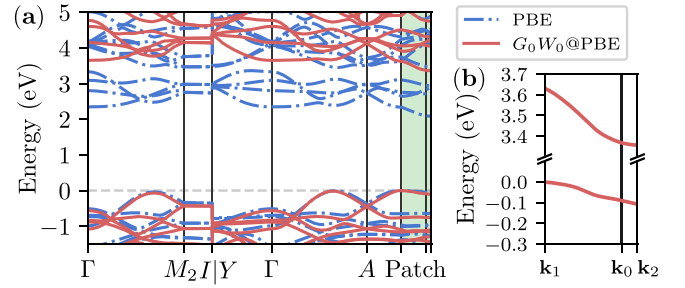


FIG. 1. Electronic band structure of m-BiVO₄. (a) PBE and G_0W_0 @PBE bands along high-symmetry paths as well as within the patch in which the BSE is solved. (b) The same path as in the green box in panel (a) shows the valence band maximum, direct gap, and the conduction band minimum. In crystal coordinates, the labeled points are $\mathbf{k}_1 = [1/24, -1/24, 9/32]$, $\mathbf{k}_0 = [1/6, -1/6, 1/8]$, and $\mathbf{k}_2 = [1/6, -5/24, 3/32]$.

but slightly smaller than eigenvalues along the high-symmetry paths. Our results indicate a direct-indirect gap difference of 0.10 eV, in agreement with the measured direct-indirect gap difference of ~ 0.1 – 0.2 eV [37]. We also find this trend holds when using local-density approximation [68,86] as a starting point (Sec. S1.5 in the Supplemental Material [53]).

Next, we solve the *ab initio* BSE in a small volume, or *patch*, in the BZ on a dense $\mathbf{k}$ grid centered at $\mathbf{k}_0$, the $\mathbf{k}$ point with the smallest G_0W_0 @PBE direct gap [85] [Fig. 1(b)], and where the lowest-lying exciton wavefunction is centered in reciprocal space. Initially neglecting K^{ph} , i.e., the clamped-ion limit, we find the lowest optical excitation energy Ω_0^S is 3.35 eV, implying $E_g^d - \Omega_0^S = 0.10$ eV, a value consistent with prior work [16,19] and the same as our G_0W_0 @PBE direct-indirect gap difference. In this work, we define the exciton binding energy as $E_B^S = \sum_{\text{cvk}} |A_{\text{cvk}}^S|^2 (E_{\text{ck}} - E_{\text{vk}}) - \Omega_0^S$, following, e.g., Ref. [87], where, instead of referencing the lowest direct gap, the reference is a weighted average of the energy of each direct transition contributing to the exciton wavefunction. This definition yields a larger binding energy of 150 meV and is expected to be more representative of the strength of the electron-hole interaction. We emphasize that this definition of E_B has no effect on our computed linewidths.

Then, we consider the effects of phonon screening by including K^{ph} . Our calculation of the orientationally averaged static dielectric constant ϵ_0 yields a large phonon contribution, with $\epsilon_\infty = 7.2$ and $\epsilon_0 = 77$. Following Refs. [41,42], the large lattice contribution, combined with the clamped-ion exciton binding energy and typical zone-center phonon frequencies in range ~ 10 – 100 meV, suggests a large binding energy renormalization due to phonon screening. Indeed, after reevaluating the BSE to include K^{ph} via Eqs. (2) and (3), we obtain an exciton energy of $\text{Re}\{\tilde{\Omega}^S\} = 3.31$ eV at zero temperature, corresponding to a 0.04 eV (or a 27%) reduction in binding energy versus the clamped-ion result. Figure 2 shows that this phonon-induced screening becomes especially pronounced at higher temperatures. Notably, at room temperature, $\text{Re}\{\tilde{\Omega}^S\}$ increases by 117 meV relative to Ω_0^S , indicating a substantial $\sim 80\%$ reduction of the exciton binding energy, and consistent with polar phonons possessing energies low enough to be activated with temperatures on the order of $k_B T \sim 20$ meV.

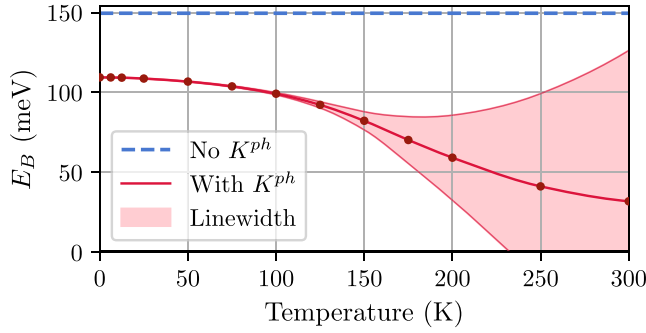


FIG. 2. Computed binding energies E_B of the first exciton vs temperature. In blue is the ion-clamped *ab initio* BSE value. The results from solving Eq. (3) are plotted in red; the linewidth from the imaginary part of $\tilde{\Omega}^S$ is overlaid as well.

This large reduction also implies the exciton energy now lies in the continuum above the direct gap, opening up the possibility of direct gap ($|\mathbf{q}| \sim 0$) emission-driven dissociation at these temperatures, as shown in Sec. S5 in the Supplemental Material [53].

The large reduction in E_B via phonon screening predicted here can be rationalized by considering the relatively low frequencies of many of the 15 zone-center polar phonons, all of which are in the range 8–107 meV. In particular, the lower frequency phonon modes contribute comparably with the highest LO mode to the overall magnitude of the real part of K^{ph} (Sec. S6 in the Supplemental Material [53]). The large impact of phonon screening on the exciton binding energy is consistent with prior work demonstrating large electron-phonon coupling and the concomitant significant reduction of the fundamental band gap [16]. We also compute the electron-phonon renormalization of the fundamental band gap to be similarly large in Sec. S3.2 in the Supplemental Material [53].

B. Exciton lifetime

Figure 2 shows the results of our *ab initio* calculations of the linewidth corresponding to phonon-driven exciton dissociation into free electrons and holes for the first exciton; it increases significantly with temperature, indicating a rapid decrease in the exciton lifetime. This trend is further illustrated in Fig. 3 that plots the lifetime of the lowest-lying exciton as a function of temperature. Remarkably, even at zero temperature, the exciton has a finite and relatively short lifetime of 6 ps, a consequence of the favorable conditions for phonon emission-driven exciton dissociation in m-BiVO₄. This is in contrast to direct gap semiconductors, where nonresonant excitons can only dissociate at finite temperatures via phonon absorption.

With increasing temperature, the dissociation lifetime decreases dramatically due to contributions from both phonon emission and absorption processes. By 100 K, it falls below 1 ps, and beyond 200 K it reaches the single-digit femtosecond regime with a computed room-temperature value of 3 fs. This is markedly smaller than measured and computed dissociation lifetimes for other semiconductors such as GaN [42], CH₃NH₃PbI₃ [88], or GaSe [89], which range between ~ 50 and ~ 100 fs.

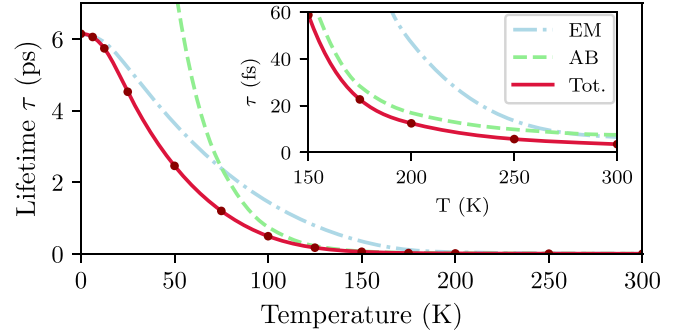


FIG. 3. Computed lifetimes for the first exciton vs temperature. At 0 K, the lifetime is entirely emission driven, and at finite temperatures the absorption channel becomes active.

For comparison, we estimate the timescales of two other major exciton scattering processes that can compete with exciton dissociation in m-BiVO₄: the bulk radiative lifetime due to electron-hole recombination and phonon-driven scattering between one bound exciton state and another. Following Ref. [43], we estimate the scattering rate of the lowest lying exciton to other higher-lying exciton states via phonon absorption and obtain a timescale at 300 K of 1 ps, a value that is comparable to, if not somewhat larger than, exciton-exciton scattering lifetimes computed for other systems in literature [43,90–92]. Following Ref. [93], we also estimate the radiative recombination lifetime of m-BiVO₄ at 300 K to be 1 ns, a timescale that is much greater than both exciton scattering and dissociation and in line with previously reported measurements in bulk semiconductors at room temperature [94,95]. Appendix C contains the details of these calculations. Taken together, these results suggest that despite clamped-ion calculations suggesting m-BiVO₄ has a strongly bound in-gap exciton, once phonon screening is taken into account, this binding energy becomes much smaller. Moreover, it strongly suggests that the dissociation of photogenerated excitons into free electrons and holes in m-BiVO₄ is a rapid and dominant process at and below room temperatures.

C. Optical absorption spectrum

The effects of electron-phonon interactions in m-BiVO₄ have a direct impact on its absorption spectrum. To obtain the phonon-screened line shape of the first bright exciton—which dominates the spectrum onset in the clamped-ion limit—we solve Eq. (B1), including the off-diagonal elements of $K_{SS'}^{\text{ph}}$ for the lowest 70 clamped-ion S states. Appendix D discusses the details of how this modifies the spectrum. In short, the complex eigenvalues as well as the left and right eigenvectors from diagonalizing the Hamiltonian in Eq. (B1) result in an asymmetric Lorentzian line shape, a result originally established by Toyozawa [96,97]. This new line shape, computed in the patch, is then applied to the first bright peak in the full-grid clamped-ion spectrum. Additionally, each BSE eigenvalue $\tilde{\Omega}^S$ is redshifted by $\Delta_{\text{scissor}} = 0.633$ eV; this correction combines the finite-temperature electron-phonon correction to the direct gap with an adjustment for the G_0W_0 @PBE starting-point error. In Fig. 4, we compare the directionally averaged optical

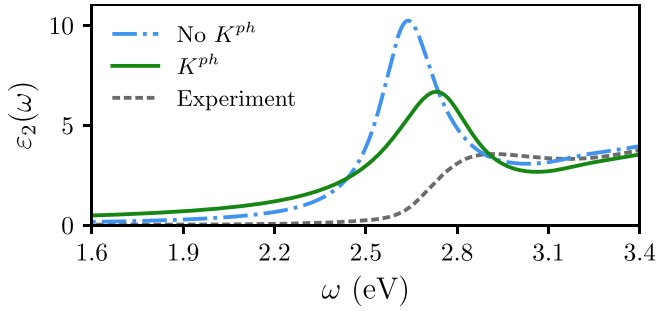


FIG. 4. Computed optical absorption spectra with and without K^{ph} with experiment [37] as reference. Corrections from K^{ph} reduce the first exciton peak height and blueshift it, leading to an onset with closer agreement to experiment.

absorption spectrum at 300 K computed with and without phonon screening; for reference, we also include the experimentally measured spectrum [37]. Relative to clamped-ion calculations, K^{ph} blueshifts the first exciton peak and reduces its height by mixing its wavefunction with other states and by increasing its broadening. Overall, these changes result in a spectrum with an exciton peak more similar to experiment, though further broadening from additional scattering channels would likely bring the spectrum into even closer accord with experiment.

IV. CONCLUSION

In summary, in this work we compute from first principles the effects of phonon screening on the lowest-lying excitons in the monoclinic phase of BiVO_4 . We find that the binding energy of the lowest lying exciton is reduced by 27% at zero temperature and nearly 80% at room temperature. We also predict exciton dissociation into free carriers on ultrafast timescales. At zero temperature, the lifetime due solely to phonon emission is on the order of picoseconds, while at room temperature the lifetime shortens to just a few femtoseconds. These findings significantly reduce the discrepancy between experiment and previous clamped-ion calculations, which predict a relatively large exciton binding energy. This rapid dissociation is estimated to outpace other bulk scattering and recombination channels, facilitating efficient free-carrier photogeneration in m- BiVO_4 . Additionally, once phonon screening is accounted for, our calculated optical absorption spectrum shows improved agreement with experiment. We expect ultrafast low-temperature exciton dissociation via phonon emission can be a general phenomenon in indirect gap materials with strong electron-phonon coupling, especially when the valence and/or conduction band extrema lie near the direct gap in the Brillouin zone. Overall, these findings underscore the key role phonon screening can play in accurate and predictive calculations of the optical properties of complex semiconductors with strong electron-phonon coupling.

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DATA AVAILABILITY

The data supporting this study's findings are available within the article.

APPENDIX A: PHONON EMISSION-DRIVEN DISSOCIATION

The basic conditions leading to a finite linewidth in Eq. (4) are determined by considering the arguments of the delta functions in the same expression. Focusing on the emission channel (−) of the first delta function, it must hold that $\omega_{\mathbf{k}-\mathbf{k}',\nu} = \tilde{\Omega}^S - (E_{\mathbf{c}\mathbf{k}} - E_{\mathbf{v}\mathbf{k}'})$. Because $\omega_{\mathbf{k}-\mathbf{k}',\nu}$ is bounded from below by 0 and from above by $\omega_{\text{LO}}^{\text{max}}$, there can only be emission from this channel if $\omega_{\text{LO}}^{\text{max}} \geq (E_{\mathbf{c}\mathbf{k}} - E_{\mathbf{v}\mathbf{k}'}) - \tilde{\Omega}^S \geq 0$. In the case of a direct gap system, unless $\tilde{\Omega}^S$ lies above the direct gap, $\tilde{\Omega}^S - (E_{\mathbf{c}\mathbf{k}} - E_{\mathbf{v}\mathbf{k}'})$ will always be negative, meaning emission cannot occur as shown in Fig. 5(a).

If the band gap is indirect, however, phonon emission-driven dissociation becomes possible even for states where $\tilde{\Omega}^S$ is below the direct gap since $\tilde{\Omega}^S - (E_{\mathbf{c}\mathbf{k}} - E_{\mathbf{v}\mathbf{k}'})$ can be positive, as shown in Fig. 5(b). The minimal value of this expression is $\tilde{\Omega}^S - E_{\text{g}}^{\text{ind}}$, where $E_{\text{g}}^{\text{ind}}$ is the indirect band gap, so as long as $\tilde{\Omega}^S \geq E_{\text{g}}^{\text{ind}}$, dissociation via phonon emission is allowed. When the difference between $\tilde{\Omega}^S$ and $E_{\text{g}}^{\text{ind}}$ is small, only low-energy phonons can be emitted, but as the difference grows, the allowed phonon energies do as well.

It is worth noting that the above constraint is necessary but not sufficient for emission-driven dissociation. Phonon dispersions are not flat and they do not necessarily span the entire energy range between 0 and $\omega_{\text{LO}}^{\text{max}}$. Ultimately, a careful consideration of both energy and momentum conservation for each state must be applied, motivating the utility of *ab initio* calculations. We also note that the same logic as above can be applied to analyze the other delta function in Eq. (4), and the same constraints emerge.

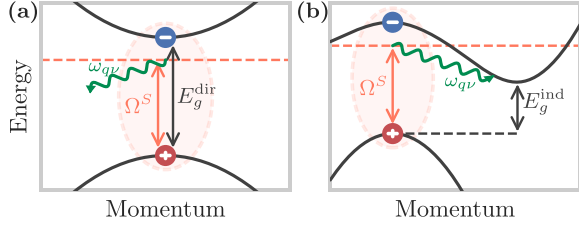


FIG. 5. Dissociation via phonon emission in (a) direct and (b) indirect band gap systems.

APPENDIX B: S BASIS DIAGONAL APPROXIMATION

The resulting BSE with phonon screening can be expressed in the clamped-ion exciton basis as

$$\sum_{S'} [\Omega^S \delta_{SS'} + K_{S,S'}^{\text{ph}}(\text{Re}\{\tilde{\Omega}^S\}, T)] \tilde{A}_{S'}^S = \tilde{\Omega}^S \tilde{A}_S^S. \quad (\text{B1})$$

Except when computing the optical absorption spectrum, we use the diagonal approximation to Eq. (B1). In this approximation, we set $K_{S,S'}^{\text{ph}}(\text{Re}\{\tilde{\Omega}^S\}, T) = 0$ for $S \neq S'$, yielding Eq. (3). The validity of this approximation has been assessed to be accurate for the first bright in-gap excitons of a number of systems in prior work [42]. However, we also demonstrate its validity for BiVO_4 by explicitly solving Eq. (B1) at $T = 300$ K for the first 70 S states in the clamped-ion basis. Figure 6 shows the results of solving this as the number of nonzero nondiagonal S states N_S increases. The real and imaginary parts of the renormalization of the new first exciton energy vary by 6 and 4 meV, respectively, as N_S increases from 1 to 70. Section S7 in the Supplemental Material [53] also demonstrates that the exciton wavefunction itself for this lowest-lying state converges around $N_S = 50$.

APPENDIX C: COMPETING DECAY PROCESSES

For comparison, we also compute the rate of radiative recombination as well as the rate of scattering to other higher-lying excitonic states via phonon absorption. We find both the lifetimes associated with these processes to be significantly greater than that of dissociation at room temperature. First, we compute the finite-temperature radiative recombination lifetime of the lowest exciton following Ref. [93] with the expression for the radiative recombination rate (in atomic

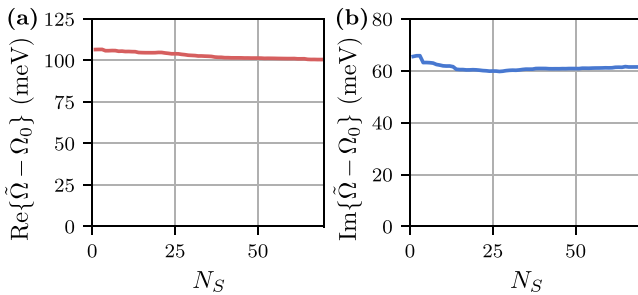


FIG. 6. Convergence of the real [panel (a)] and imaginary [panel (b)] parts of the renormalization of the exciton energy vs the size of the nondiagonal S basis (N_S) used to solve Eq. (B1) at 300 K.

units)

$$\gamma_{\text{rad}}^S = \frac{2^5 \sqrt{\pi^3 \epsilon_\infty} d_s^2}{3V} \frac{(\Omega^S \alpha)^3}{N_k (2Mk_B T)^{3/2}}, \quad (\text{C1})$$

where ϵ_∞ is the clamped-ion macroscopic dielectric constant (computed via DFPT), V is the unit cell volume, d_s^2 is the optical dipole matrix element (obtained by solving the BSE), N_k is the number of $\mathbf{k}$ points used when solving the BSE, α is the fine structure constant, and $M = m_e + m_h$ is the exciton total effective mass (computed in Sec. S3.1 in the Supplemental Material [53]). The lifetime due to radiative recombination is then simply the inverse $\tau_{\text{rad}}^S = (\gamma_{\text{rad}}^S)^{-1}$. We note that this expression assumes ϵ_∞ , M , and d_s^2 to be isotropic, which, strictly speaking, is not the case for BiVO_4 . However, as an approximation, we directionally average each quantity when using Eq. (C1). At 300 K, this approach yields a lifetime of 1 ns.

Second, we compute the scattering rate of the lowest $\mathbf{Q} = 0$, $S = 1$ exciton into other states using the model discussed at length in Ref. [43]. Specifically, a generalized Fröhlich electron-phonon coupling [100] (assuming isotropic LO-TO splitting) is used, namely,

$$g_{\nu\mathbf{q}}^F = \frac{i}{|\mathbf{q}|} \sqrt{\frac{2\pi}{N_k V \epsilon_\infty} \frac{\omega_{\text{LO}}^{\nu 2} - \omega_{\text{TO}}^{\nu 2}}{\omega_{\text{LO}}^{\nu}}}, \quad (\text{C2})$$

with ν indexing over each LO-TO splitting of polar phonon modes, to construct the exciton-phonon coupling matrix element for an optically excited (effectively zero momentum) exciton of state S [101]:

$$G_{SS'\nu}(\mathbf{0}, \mathbf{q}) = g_{\nu\mathbf{q}}^F \sum_{\mathbf{k}} A_{\mathbf{k}}^{S,\mathbf{q}*} (A_{\mathbf{k}}^{S',\mathbf{0}} - A_{\mathbf{k}+\mathbf{q}}^{S',\mathbf{0}}). \quad (\text{C3})$$

Here, $A_{\mathbf{k}}^{S,\mathbf{q}}$ is the wavefunction of an exciton with center-of-mass momentum $\mathbf{q}$ at the reciprocal lattice point $\mathbf{k}$. Due to the computational difficulty of calculating the finite center-of-mass momentum exciton wavefunctions needed to construct $G_{SS'\nu}$, we instead use hydrogenic wavefunctions for the $1s$, $2s$, $2p$, and $3s$ excitons, with the effective Bohr radius a_0^{eff} obtained by fitting the BSE exciton wavefunction for the lowest excitation in Sec S3.1 in the Supplemental Material [53]. We also assume parabolic exciton dispersions using effective masses obtained from fitting the bands at the direct gap as done in Sec. S3.1 in the Supplemental Material [53]. The scattering rate to other excitons is then calculated according to

$$\gamma_{\text{ex-ex}}^S = 2\pi \sum_{S'\mathbf{q}\nu} |G_{SS'\nu}(\mathbf{0}, \mathbf{q})|^2 \delta(\Omega^S - \Omega_{\mathbf{q}}^{S'} + \omega_{\mathbf{q}\nu}), \quad (\text{C4})$$

with the corresponding lifetime obtained via $\tau_{\text{ex-ex}}^S = (\gamma_{\text{ex-ex}}^S)^{-1}$. At 300 K, we calculate this lifetime to be 1 ps.

APPENDIX D: ABSORPTION SPECTRUM RENORMALIZATION

In order to obtain a renormalized optical absorption spectrum, we compute the complex eigenvalues and the left ($\tilde{B}_S^S$) and right ($\tilde{A}_S^S$) eigenvectors from the BSE Hamiltonian in Eq. (B1), treating $K_{S,S'}^{\text{ph}}$ as nondiagonal for the first 70 clamped-ion states (see Appendix B and Sec. S7 in the Supplemental

Material [53] for convergence). For completeness, we also show the left eigenvalue problem: Because the Hamiltonian in Eq. (B1) is non-Hermitian, the left and right eigenvectors are not Hermitian conjugates, but they are normalized to satisfy biorthonormality ($\sum_S \tilde{B}_S^{\tilde{S}} \tilde{A}_S^{\tilde{S}'} = \delta_{\tilde{S}\tilde{S}'}$). The square of the clamped-ion dipole matrix element [49,50] along the polarization direction i , $r_S^i = \sum_{\mathbf{cvk}} (A_{\mathbf{cvk}}^S)^* \langle \mathbf{v} | \mathbf{k} | \mathbf{c} \rangle$, is accordingly transformed [47,50,91] to give

$$D_S^i = \sum_{S'} r_S^{i*} \tilde{A}_S^{\tilde{S}} \tilde{B}_{S'}^{\tilde{S}} r_{S'}^i. \quad (\text{D1})$$

The renormalized optical spectrum with only broadening from K^{ph} dissociation channels is then

$$\begin{aligned} \tilde{\varepsilon}_2^i(\omega) = 8\pi^2 \sum_{\tilde{S}} \frac{\text{Re}\{D_S^i\} \text{Im}\{\tilde{\Omega}^{\tilde{S}}\}}{(\omega - \text{Re}\{\tilde{\Omega}^{\tilde{S}}\})^2 + \text{Im}\{\tilde{\Omega}^{\tilde{S}}\}^2} \\ + \frac{\text{Im}\{D_S^i\}(\omega - \text{Re}\{\tilde{\Omega}^{\tilde{S}}\})}{(\omega - \text{Re}\{\tilde{\Omega}^{\tilde{S}}\})^2 + \text{Im}\{\tilde{\Omega}^{\tilde{S}}\}^2}. \end{aligned} \quad (\text{D2})$$

This asymmetric form of the spectrum coming from $\text{Im}\{D_S^i\}$ due to exciton-phonon coupling is rarely calculated *ab initio* (to our knowledge, only Ref. [91] reports a comparable calculation), but has been long established by Toyozawa [96,97]. This definition of $\tilde{\varepsilon}_2(\omega)$ affects the strength of dipole matrix elements, going beyond simply shifting the exciton energies as is done in Ref. [99].

In practice, we add a uniform background width of 100 meV to the state-resolved linewidths from K^{ph} in order to account for residual scattering and finite $\mathbf{k}$ -point sampling. We also apply an additional scissor shift Δ_{scissor} to all $\tilde{\Omega}^{\tilde{S}}$

used to calculate $\tilde{\varepsilon}_2(\omega)$. This shift contains two corrections. The first is the renormalization of the lowest direct band gap at 300 K due to electron-phonon coupling, as discussed in Sec. S3.2 in the Supplemental Material [53]; this correction is -0.933 eV. The second correction accounts for the band gap starting-point error of G_0W_0 @PBE; as was shown in Ref. [19], G_0W_0 calculation in BiVO_4 that uses a nonempirical optimally tuned hybrid functional [98] increases the band gap by 0.30 eV relative to G_0W_0 @PBE. Thus, in total, we apply a redshift of $\Delta_{\text{scissor}} = 0.633$ eV to our spectra.

In order to extend the spectrum computed in Eq. (D2) to account for more than the first 70 states, we also plot the conventional clamped-ion BSE spectrum,

$$\varepsilon_2^i(\omega) = 8\pi^2 \sum_{S>70} |r_S^i|^2 \delta(\omega - \Omega^S), \quad (\text{D3})$$

for the higher-lying states. In this case, the delta functions are replaced with Lorentzian envelopes with broadening of 100 meV as above.

Finally, because the renormalized spectrum computed for a BZ patch cannot be mapped unambiguously onto the full-grid calculation, we confine our analysis of the effects of K^{ph} in Fig. 4 to the first bright exciton that dominates the clamped-ion full-grid spectrum onset. We therefore only use the spectrum from Eq. (D2) for this first bright peak and then use Eq. (D3) for all the rest of the states. Consequently, the redistribution of exciton oscillator strength to other states in the full-grid calculation is neglected. However, this redistribution of weight is relatively uniform for states in the patch.

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