Frenkel Biexciton binding and many-body contributions to exciton line-shapes

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VISTA Webseminar: May 25, 2021

Quantum Entanglement Spectroscopy & manybody effects in 2d coherent spectroscopy

- ⋆ Quantum Light Emission from Coupled Defect States in DNA-Functionalized Carbon Nanotubes, Zheng, Yu; Kim, Younghee; Jones, Andrew; Olinger, Gabrielle; Bittner, Eric; Bachilo, Sergei; Doorn, Stephen; Weisman, R. Bruce; **A Piryatinski**; Htoon, Han, Submitted to Advanced Materials. 8-Feb-2021
- ⋆ Photon Supersqueezing: exact eigenstates of the generalized squeezing operator, Andrey Pereverzev, and Eric R. Bittner, Journal of Physics B: Atomic, Molecular and Optical Physics. Submitted 8-Feb-2021.
- ⋆ The molecular origin of Frenkel biexciton binding Elizabeth Gutierrez Meza, Ravyn Malatesta, Hongmo Li, Ilaria Bargigia, Ajay Ram Srimath Kandada, David A. Valverde-Chavez, Natalie Stingelin, Sergei Tretiak,Eric R. Bittner, and **Carlos Silva**, Science Advances, arXiv preprint arXiv:2101.01821
- ⋆ Probing exciton/exciton interactions with entangled photons:theory, Eric R. Bittner, Hao Li, **Andrei Piryatinski**, Ajay Ram Srimath Kandada, **Carlos Silva** J. Chem. Phys. 152, 071101 (2020)
- ⋆ Non-equilibrium states of a plasmonic Dicke model with coherent and dissipative surface plasmon-quantum emitter interactions, **A Piryatinski**, Oleksiy Roslyak, Hao Li, Eric R. Bittner, Phys. Rev. Research. 2, 013141 (2020).
- ⋆ Stochastic scattering theory for excitation induced dephasing: Comparison to the Anderson-Kubo lineshape Hao Li, Ajay Ram Srimath Kandada, **Carlos Silva**, Eric R. Bittner J. Chem. Phys. 153, 154115 (2020) arXiv preprint arXiv:2008.09218
- ⋆ Stochastic scattering theory for excitation induced dephasing: Time-dependent nonlinear coherent exciton lineshapes ARS Kandada, H Li, F Thouin, ER Bittner, **C Silva** J. Chem. Phys. 153, 164706 (2020) arXiv preprint arXiv:2008.08211

Keeping sane during the pandemic.

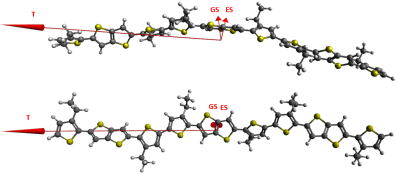
in addition, I built a sail boat in my garage...

...and practiced social distancing.

Overview of topics

Ideas/theories related to detecting many-body dynamics and correlations in excitonic materials

- ⋆ Attractive and repulsive bi-exciton states in H- and J-aggregates
- ⋆ Dephasing dyamics due to non-stationary background excitations.
- ⋆ Detecting bi-excitons with quantum light.



PBTTT:

Biexcitons: consequential intermediates:

* exciton dissociation into electrons (e^-) and holes (h^+)
  $S_0 + 2\hbar\omega \longrightarrow [2S_1]^\ddagger \longrightarrow 2\,e^- + 2\,h^+$
* bimolecular annihilation
  $S_1 + S_1 \longrightarrow [2S_1]^\ddagger \longrightarrow S_0 + S_0$
* singlet fission producing triplet (T_1) states
  $S_0 + 2\hbar\omega \longrightarrow [2S_1]^\ddagger \longrightarrow 2\,T_1 + 2\,T_1$

In each of these we see the biexciton $[2S_1]^\ddagger$ as some form of transition state.

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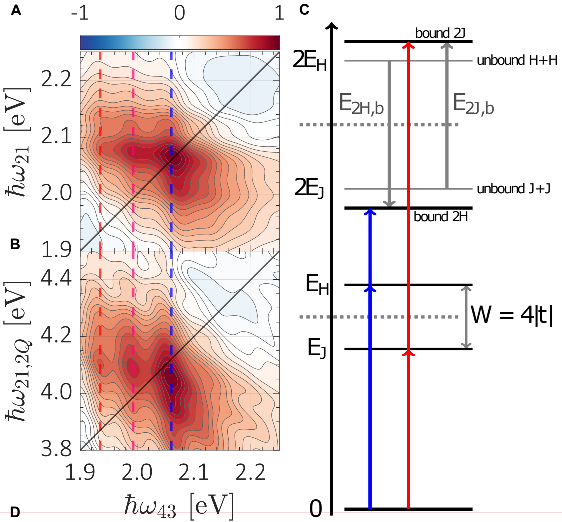
[1] Science Advances, ArXiv:2101.01821

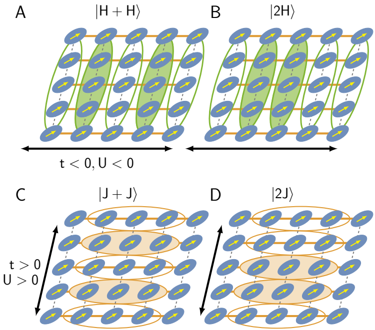
Evidence: from Carlos Silva's group

2d-coherent & 2d coherent double quantum spectra



H vs. J biexcitons

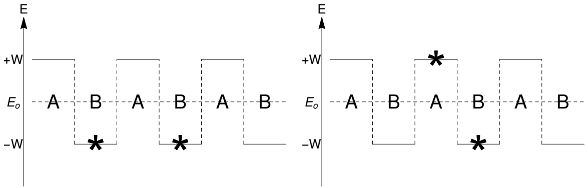
Possible states:



* H-excitons: aligned ⊥ to chain, move ∥ along chain
* J-excitons: aligned ∥ to chain, move ⊥ to the chains

Focusing on the 1D motion of the exciton state:

$$\hat{H} = E_0 + \Delta \sum_{j=1}^{N} (-1)^j \hat{c}_j^\dagger \hat{c}_j + t \sum_{j=1}^{N} (\hat{c}_j^\dagger \hat{c}_{j+1} + \hat{c}_{j+1}^\dagger \hat{c}_j)$$
$$+ U \sum_{j=1}^{N} \hat{c}_j^\dagger \hat{c}_j \hat{c}_{j+1}^\dagger \hat{c}_{j+1}. \quad (1)$$



Crenelation + noise: $w = \Delta + \delta\Delta_n$

Set $t = -\hbar^2/2\mu$ and U as the contact interaction.

$$t\frac{d^2\psi(x)}{dx^2} + U\delta(x)\psi(x) = E\psi(x). \quad (2)$$

Solutions: Taking $E/t = \kappa^2$

$$\psi(x) = \sqrt{\kappa}e^{-\kappa|x|} \quad (3)$$

Typical case: $t < 0$ and $U < 0$ produce a single state energetically below the $E > 0$.
But $t > 0$ and $U > 0$ also produce bound state. Possible if $\mu < 0$

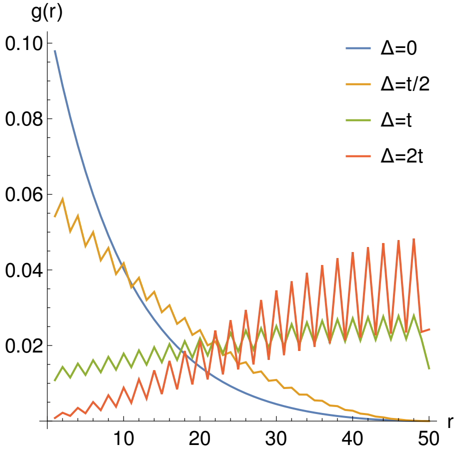


Figure – Exciton/exciton radial distribution $g^{(2)}(r_1 - r_2)$ from 1D lattice model for increasing crenelation.

Free vs. bound excitons: $t < 0$ and $U < 0$

parametric threshold for formation of bound excitons[2]

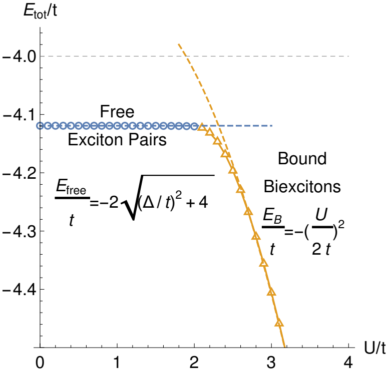


Figure – Free vs. bound biexciton energies.

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[2](turn upside down for $t > 0$ and $U > 0$ case!)

Biexcitons obey current social norms

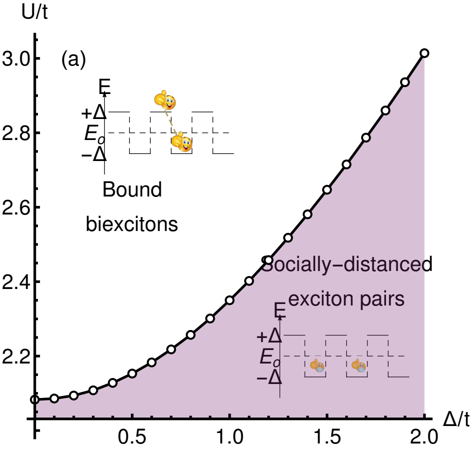


Figure – Phase diagram for Biexcitons

Inclusion of static (energetic) disorder

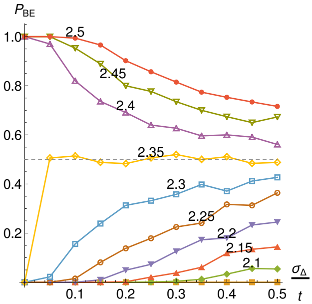
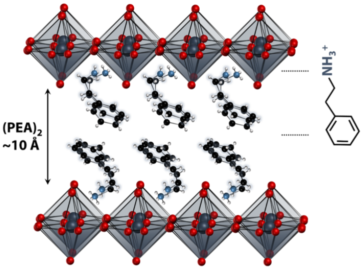
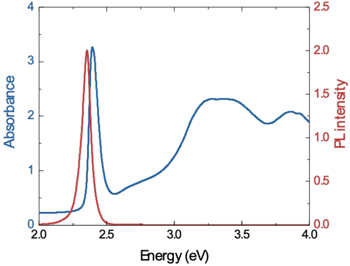


Figure – Probability of biexciton formation for disordered lattices. Curves are labeled by the interaction U for $U/t = 2.5$ to $U/t = 2.1$

Summary

- ⋆ First detection (that we're aware of) of repulsive and attractive bound bi-exciton states in same material.
- ⋆ Model suggests that both kinds of biexcitons should be detectable in a wide range of materials as tuned by exciton interaction and hopping integrals.
- ⋆ *Robust* against static lattice noise, although disorder may cause local traps





Road map: excitons in 2D perovskites

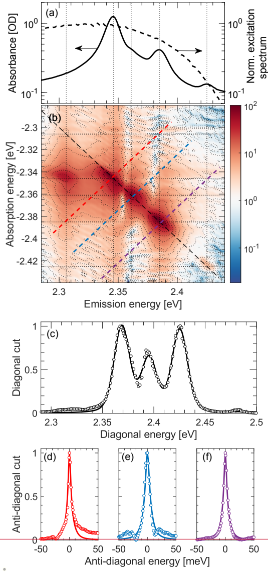
Linear spectral lineshape — spectral structure

Exciton polaron effects

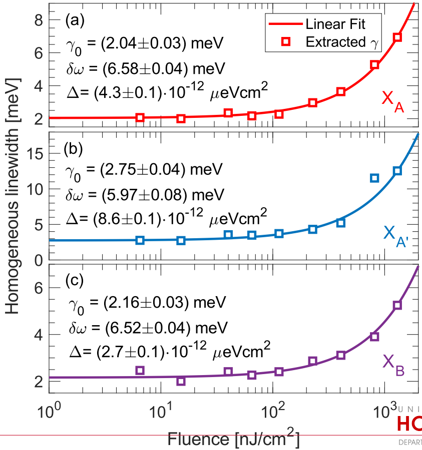
Nonlinear spectral lineshape — dephasing

A.R. Srimath Kandada, C. Silva, *J. Phys. Chem. Lett.* **11**, 3173–3184 (2020)

Excitation-density-dependent dephasing rate



$$\gamma(n) = \gamma_0 + \Delta \cdot n$$



Thouin et al., Phys. Rev. Research **1**, 032032(R)

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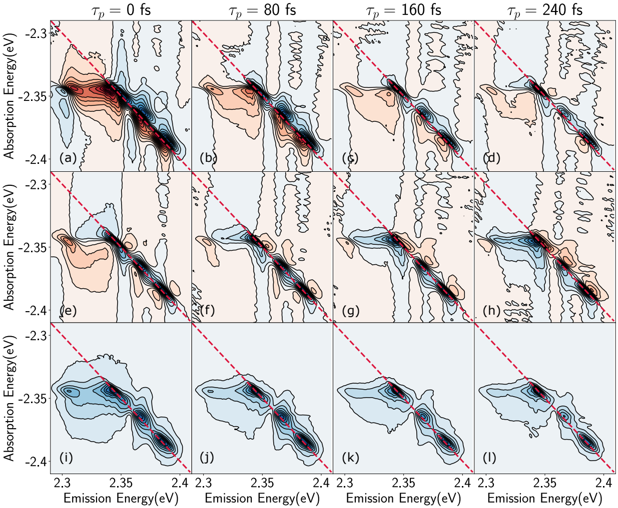
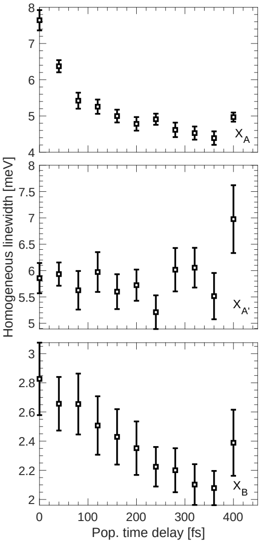
2D coherent excitation lineshape ($T = 5\,\mathrm{K}$)

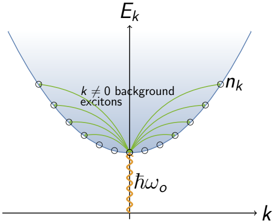


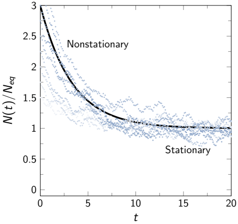
Thouin et al., Phys. Rev. Research **1**, 032032(R) (2019)

2D coherent excitation lineshape ($T = 5\,\mathrm{K}$)



In low-dimensional/solid state systems, one has local field effects due to background excitations viz. $\delta n(r) = dD(\epsilon_F)\delta U(r)$, which leads to a screening length.





Narrow excitation pulse widths ⇝ broad band excitation ⇝ transient local field effects.

[3] J. Chem. Phys. 153, 154115 (2020); J. Chem. Phys. 153, 164706 (2020)

We start from many-body exciton theory:[4]

$$H = \int \frac{\hbar^2}{2m}(\nabla\hat{\psi}^\dagger)(\nabla\hat{\psi})dr + \frac{1}{2}\int dr dr' \hat{\psi}^\dagger(r')\hat{\psi}^\dagger(r)V(r-r')\hat{\psi}(r')\hat{\psi}(r) \quad (4)$$

After some (hopefully) well justified approximations,we arrive at an *effective* Hamiltonian (with $\hbar = 1$)

$$H_0(t) \approx \omega_0 a_0^\dagger a_0 + \frac{V_o}{2} a_0^\dagger a_0^\dagger a_0 a_0 + 2V_o a_0^\dagger a_0 N(t) \quad (5)$$

with $N(t)$ giving the inst. population of background excitations.

[4] The form of the exciton/exciton interaction doesn't matter for s-wave scattering since I can replace the true potential with a fictitious potential with same scattering length.

Model: background excitations $N(t)$ scatter from $k = 0$ excitons and create energy gap fluctuations (similar to Kubo/Anderson)
Exciton (system) operators:

$$\hat{a}_0(t) = \exp\left\{ \left(-i(\omega_0 + \frac{V_o}{2}\hat{n}_0)t - i2V_o \int_0^t N(\tau)d\tau \right) \right\} \hat{a}_0 \equiv \hat{U}(t)\hat{a}_0, \tag{6}$$

Postulate: $N(t)$ follows an Ornstein/Uhlenbeck process.

$$dN = -\gamma N dt + \sigma dW \tag{7}$$

where $(dW(t))^2 = dt$ (from Ito Calculus)
This gives $\langle N(t) \rangle = N_o e^{-\gamma t}$.

Linear responses ($\gamma_1 = 2V_o$)

$$\langle \hat{a}_0(t)\hat{a}_0^\dagger(0)\rangle = \left\langle a_0(0)a_0^\dagger(0)\exp\left[-i\omega_o t - i\gamma_1\int_0^t d\tau N(\tau)\right]\right\rangle \quad (8)$$

$$\langle \hat{a}_0^\dagger(t)\hat{a}_0(0)\rangle = \left\langle a_0^\dagger(0)a_0(0)\exp\left[+i\omega_o t + i\gamma_1\int_0^t d\tau N(\tau)\right]\right\rangle \quad (9)$$

Need to be careful in evaluating the cumulants,

$$\left\langle e^{-i\gamma_1\int_0^t d\tau N(\tau)}\right\rangle = e^{-i\gamma_1\int_0^t d\tau\langle N(\tau)\rangle}e^{-\frac{\gamma_1^2}{2}\int_0^t d\tau_1\int_0^t d\tau_2\langle N(\tau_1)N(\tau_2)\rangle} \quad (10)$$

$$= e^{-i\gamma_1 g_1(t)}e^{-\gamma_1^2 g_2(t)/2} \quad (11)$$

since the covariance $\langle N(t)N(t')\rangle \neq \langle N(t-t')N(0)\rangle$ since we're dealing with a non-stationary ensemble.

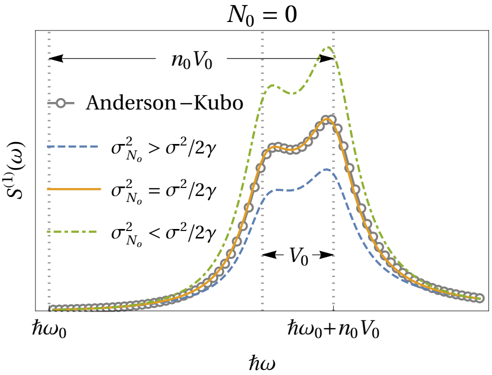


Figure – The linear response function comparison between the non-stationary and the Anderson-Kubo (AK) model in the case of zero initial background population N_0 at different distributions $\sigma_N^2 = 0.25$, 0.125, and 0.04 fs^{-1}. Other parameters are $V_o = 10$ meV, $\gamma = 0.01$ fs^{-1}, $\sigma^2 = 0.0025$ fs^{-1}.

Non-stationary background

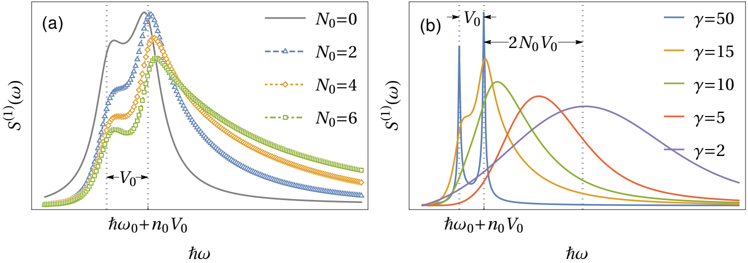


Figure – The linear response function with (a) increasing background population density N_0, and (b) different relaxation rate γ, from the homogeneous limit of $\gamma = 50$ meV to the inhomogeneous limit of $\gamma = 2$ meV.

Model features

Blocking: Increasing the initial background suppresses the peak absorption intensity.

Energy shift: The peak position shifts to the blue with increasing background population due to increased Coulombic interactions.

Broadening: The spectrum acquires a long tail extending to the blue due to the dynamical evolution of the background. This feature also appears in the 2D coherent spectroscopy as an asymmetry along the absorption axis and as phase scrambling in the rephasing and non-rephasing signals. [**?**]

Biexciton: The peak is split by V_0 corresponding to the biexciton interaction.

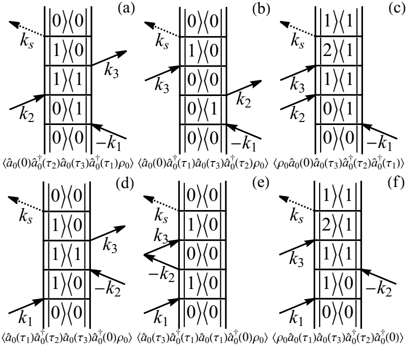


Figure – Double-sided Feynman Diagrams for coherent response functions with rephasing phase matching (top): (a) R_{2a}, (b) R_{3a}, (c) R_{1b}^*, and non-rephasing phase matching (bottom): (d) R_{1a}, (e) R_{4a}, (f) R_{2b}^*.

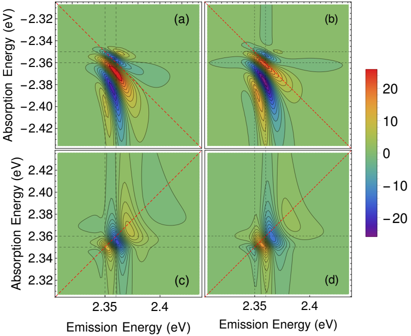


Figure – Theoretical real and imaginary spectra, respectively, of rephasing [(a), (b)] and nonrephasing [(c), (d)] phase matching and at population waiting time $\tau_p = 0\,\text{fs}$. The vertical false color scale indicated to the right if the figure is in arbitrary units.

Evolution of rephasing peak

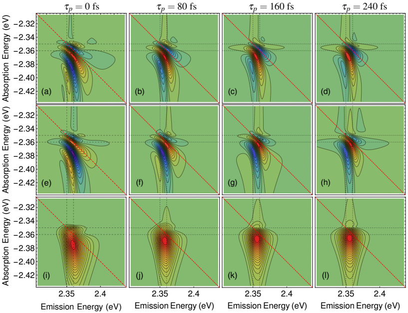


Figure – (a)–(d): Real parts of theoretical rephasing spectra at population times τ_p indicated at the top of each panel. (e)–(h): Corresponding imaginary parts of the spectrum. (i)–(l): The norm (absolute value) of the optical response.

Evolution of rephasing peak

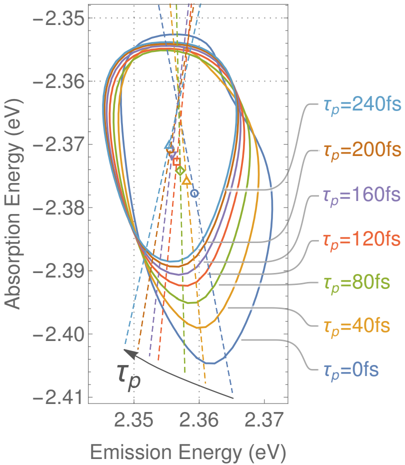


Figure – Exciton 2D coherent lineshape contour at half-maximum intensity as a function of population waiting time derived from the theoretical rephasing absolute spectral evolution in Fig. 9. The center of mass and one of the principle axes are shown for each contour.

Summary

Model gets it right!

Summary

- ⋆ Stochastic model for background-induced dephasing/energy shifts.
  - ⊗ Use of Ito calculus + SDE to model nonstationary background exciton population.
  - ⊗ Can extend to more correlated noise models (Hao Li + ERB, in prep).
  - ⊗ Numerical: use methods from qualitative finance!
- ⋆ Frenkel Biexcitons
  - ⊗ Long predicted (Agranovich, 60's)
  - ⊗ Readily seen in quantum dots (Wannier excitons)
  - ⊗ Both 2J and 2H species seen in same sample!

Acknowledgements

- ⋆ **Dr. Hao Li (Univ. of Houston)**
- ⋆ **Prof. Carlos Silva (Georgia Tech)**
- ⋆ **Dr. Andrei Piryatinski (LANL)**
- ⋆ **Dr. Ajay Ram Srimath Kandada (IIT. Milano)**
- ⋆ **Dr. Jonathan Jerke (Texas Tech Univ.)**

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Recent group papers

* Photon supersqueezing: exact eigenstates of the generalized squeezing operator Andrey Pereversev and Eric R. Bittner, J. Chem. Phys. special issue on Quantum Light.
* The molecular origin of Frenkel biexciton binding, Elizabeth Gutierrez Meza, Ravyn Malatesta, Hongmo Li, Ilaria Bargigia, Ajay Ram Srimath Kandada, David A. Valverde-Chavez, Natalie Stingelin, Sergei Tretiak,Eric R. Bittner, and Carlos Silva (2021)
* Stochastic scattering theory for excitation induced dephasing: Comparison to the Anderson-Kubo lineshape Hao Li, Ajay Ram Srimath Kandada, Carlos Silva, Eric R. Bittner J. Chem. Phys. 153, 154115 (2020); arXiv preprint arXiv:2008.09218
* Stochastic scattering theory for excitation induced dephasing: Time-dependent nonlinear coherent exciton lineshapes ARS Kandada, H Li, F Thouin, ER Bittner, C Silva J. Chem. Phys. 153, 164706 (2020) arXiv preprint arXiv:2008.08211

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