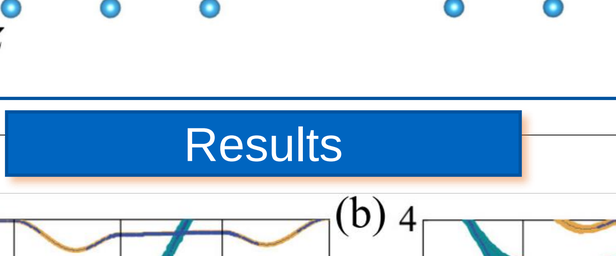
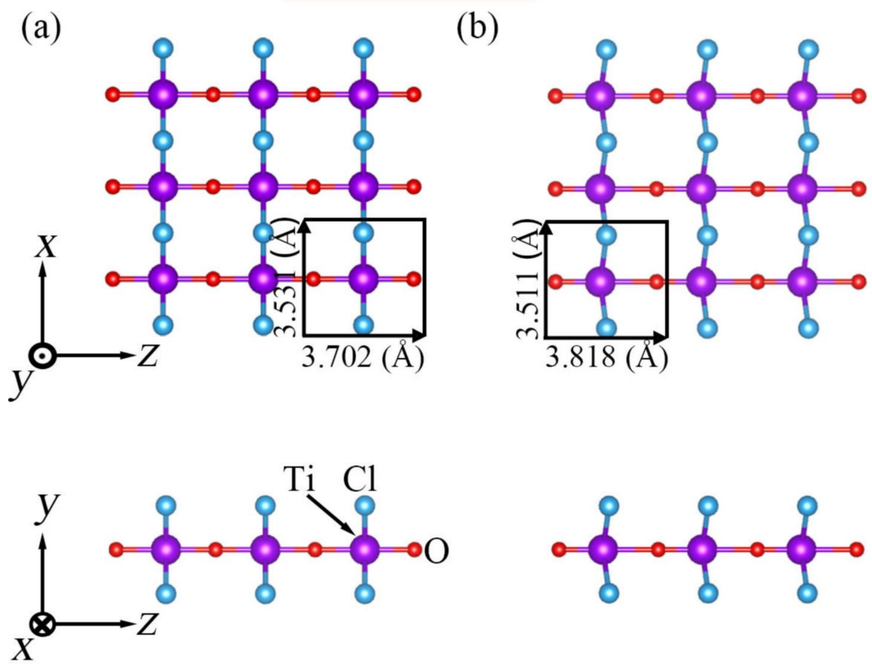
# Giant enhancement of exciton case of radiative lifetime by ferroelectric polarization: The monolayer $TiOCl_2$

## Introduction

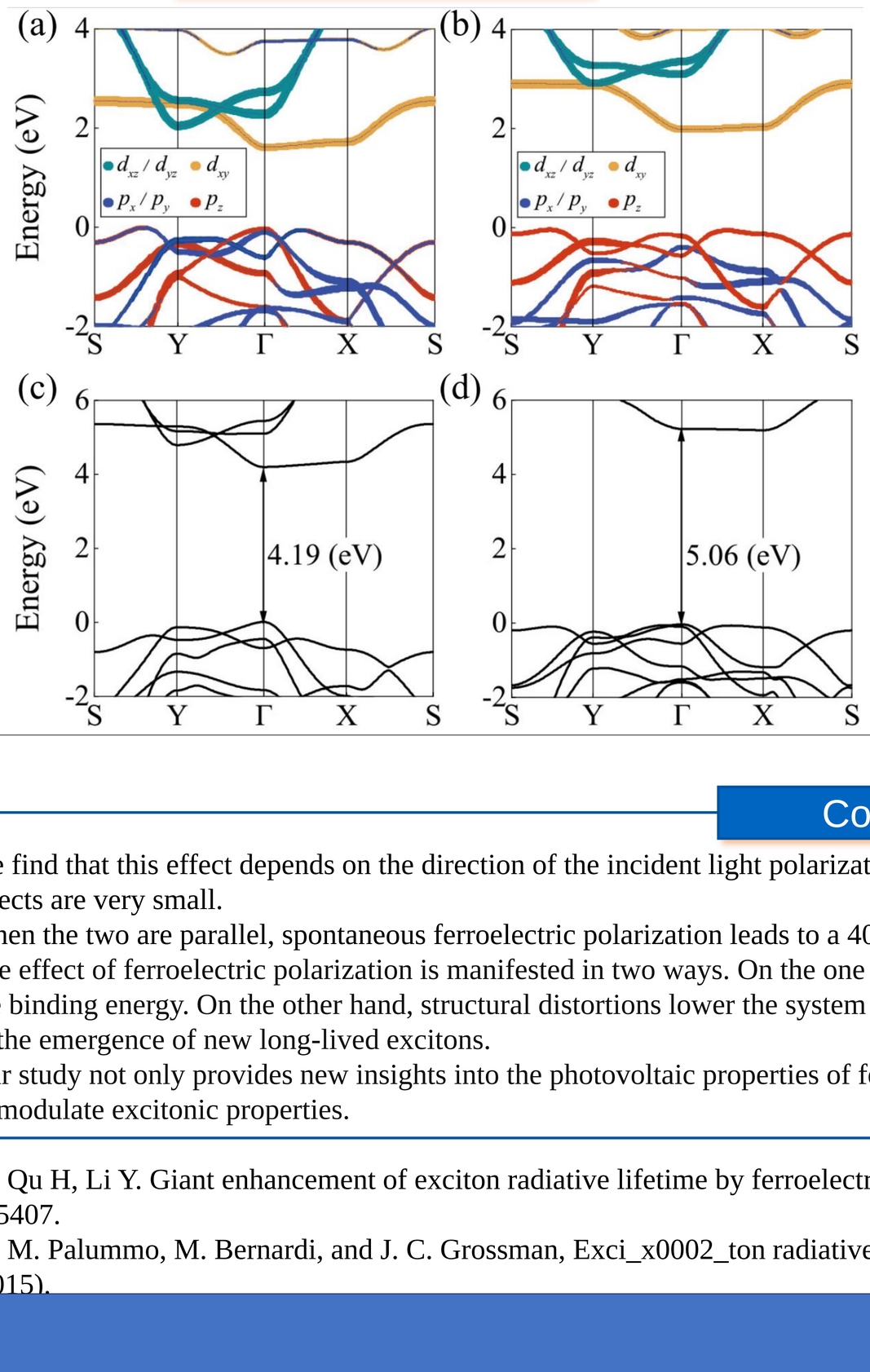
Exciton binding energy and lifetime are the two most important parameters controlling exciton dynamics, and the general consensus is that the larger the former the larger the latter. However our first-principles study of monolayer ferroelectric $TiOCl_2$ shows that this is not always the case. We find that ferroelectric polarization tends to weaken exciton binding but enhance exciton lifetime.This stems from the different effects of the induced built-in electric field and structural distortion by the spontaneous polarization: the former always destabilizes or even dissociates the exciton while the latter leads to a relaxation of the selection rule and activates excitons that are otherwise not optically active. Their combined effect leads to a halving of the exciton binding energy but a substantial increase in lifetime by 40 times.




## Models




## Results




## Calculation method

GW approximation

Bethe-Salpeter Equation (BSE)

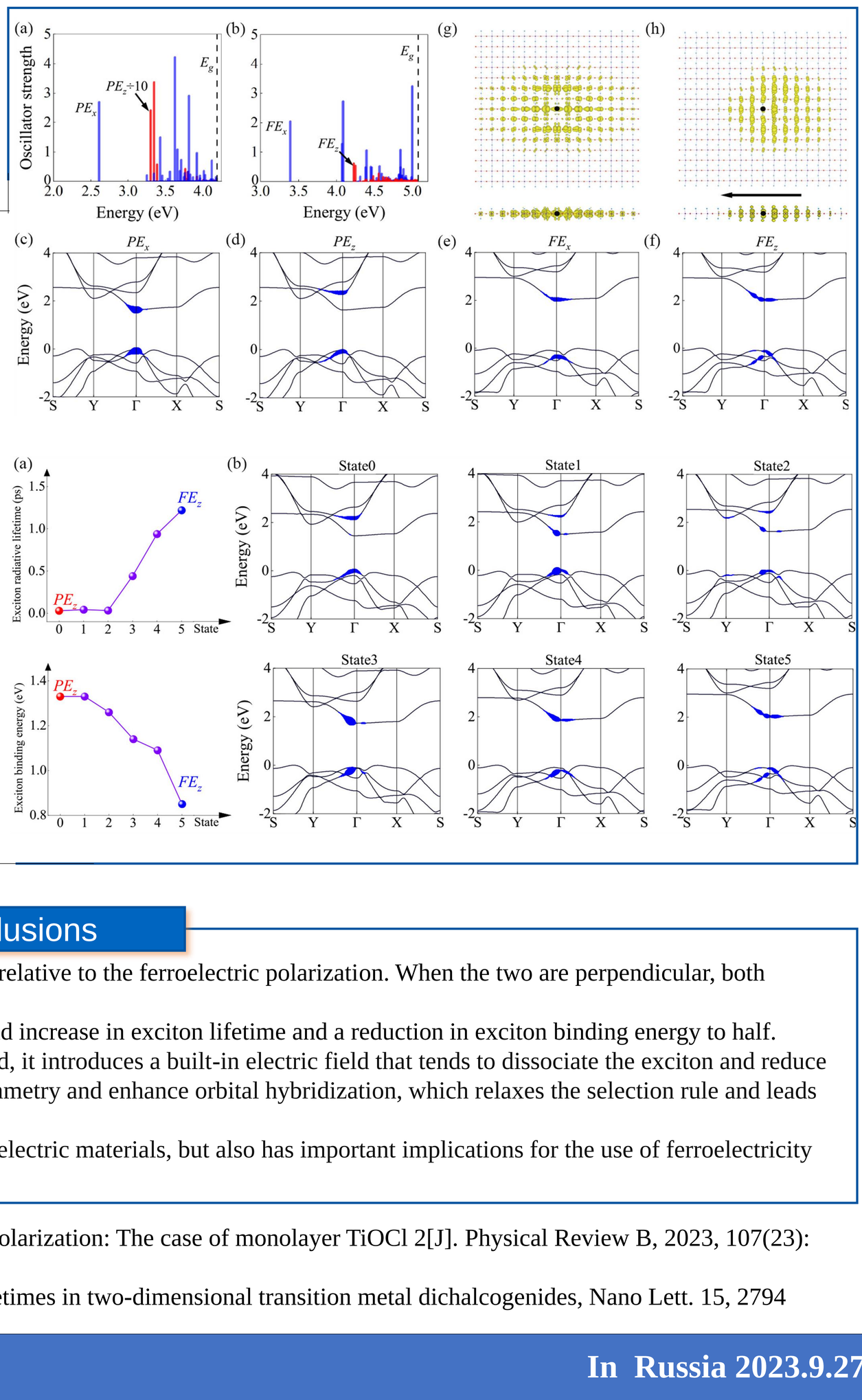
$$H^{vck}_{v'c'k'} = (\varepsilon_{ck} - \varepsilon_{vk})\delta_{vv'}\delta_{cc'}\delta_{kk'} + (f_{ck} - f_{vk})[2\bar{V}^{vck}_{v'c'k'} - W^{vck}_{v'c'k'}]$$

$$\varepsilon_M(\omega) \equiv 1 - \lim_{q\to 0} \frac{8\pi}{|q|^2\,\Omega} \sum_{vck}\sum_{v'c'k'} < vk-q\,|\,e^{-iqr}\,|\,ck >< c'k'\,|\,e^{-iqr}\,|\,v'k'-q > \sum_{\lambda} \frac{A^{\lambda}_{cvk}(A^{\lambda}_{c'v'k'})^*}{\omega - E_{\lambda}}$$

$$\gamma_S(\mathbf{Q}) = \frac{2\pi}{\hbar} \sum_{\mathbf{q},\lambda} |\langle G, 1_{\mathbf{q},\lambda}|H_{int}|S(\mathbf{Q}),0\rangle|^2\,\delta(E_S(\mathbf{Q}) - \hbar c q)$$

$$\tau = \frac{A_{\mu c}\hbar^2 c}{8\pi e^2 E_S(0)\mu_S^2} \qquad \tau = K\frac{A_{uc}}{E_S(0)\mu_S^2} \qquad K = \frac{\hbar^2 c}{8\pi e^2}$$

$$\mu_S^2 = \frac{\hbar^2}{m^2 E_S(0)^2} \frac{\left|\langle G\,|\,p_{||}\,|\,\Psi_S(0)\rangle\right|^2}{N_k}$$




## Conclusions

We find that this effect depends on the direction of the incident light polarization relative to the ferroelectric polarization. When the two are perpendicular, both effects are very small.

When the two are parallel, spontaneous ferroelectric polarization leads to a 40-fold increase in exciton lifetime and a reduction in exciton binding energy to half.

The effect of ferroelectric polarization is manifested in two ways. On the one hand, it introduces a built-in electric field that tends to dissociate the exciton and reduce the binding energy. On the other hand, structural distortions lower the system symmetry and enhance orbital hybridization, which relaxes the selection rule and leads to the emergence of new long-lived excitons.

Our study not only provides new insights into the photovoltaic properties of ferroelectric materials, but also has important implications for the use of ferroelectricity to modulate excitonic properties.


[1] Qu H, Li Y. Giant enhancement of exciton radiative lifetime by ferroelectric polarization: The case of monolayer TiOCl 2[J]. Physical Review B, 2023, 107(23): 235407.

[2] M. Palummo, M. Bernardi, and J. C. Grossman, Exci_x0002_ton radiative lifetimes in two-dimensional transition metal dichalcogenides, Nano Lett. 15, 2794 (2015).