Supporting Information: Optical images of molecular vibronic couplings from tip-enhanced fluorescence excitation spectroscopy

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S1 Selection rules for the vibrational transitions of the H$_2$P molecule

S1.1 H$_2$P in free space

The ground state of the H$_2$P molecule has the symmetry of D$_{2h}$. The molecule contains 38 atoms and has 108 vibration modes which can be written as an irreducible representation of (by assuming the molecule in the $xy$ plane)

$$\Gamma_{vib} = 19A_g + 8A_u + 8B_{3g} + 18B_{3u} + 9B_{2g} + 18B_{2u} + 18B_{1g} + 10B_{1u}.$$  \hfill (S1)

In all of the 108 modes, only the 19 totally symmetric $A_g$ modes are Franck-Condon (FC) active because for the non-totally symmetric modes we have $\langle n \mid n' \rangle = \delta_{nn'}$ due to the orthogonality of the vibrational wave functions. For the H$_2$P molecule in free space, the symmetry for the ground electronic state (S0), the first (S1) and second (S2) excited states is $A_g$, $B_{3u}$, and $B_{2u}$, respectively. As a result, both excited states are optically forbidden in the direction perpendicular to the molecular plane ($z$ direction in the present work). In this case, only the vibrational transitions that involve the Herzberg-Teller (HT) active modes are allowed. In the $z$-direction, the HT active modes for the $B_{3u}$ and $B_{2u}$ states are the $B_{2g}$ and the $B_{3g}$ modes, respectively.

S1.2 H$_2$P under the influence of SCP

As we have discussed in the main text, because we assumed the SCP to be homogeneous in the $z$ direction, both the $S_0 \to S_1$ transition ($Q_x$ band) and the $S_0 \to S_2$ transition ($Q_y$ band) will remain FC forbidden ($\mu_z^e(Q_0) = 0$). As a result, vibrational transitions contain only the FC active totally symmetric $A_g$ modes will not be present in the TEFE spectrum.

In contrast to the molecule in free space, the spatial confinement of the SCP makes the TEFE measures effectively the local vibronic couplings. In this case, not only the $B_{2g}$ for
$Q_x$ and $B_{3g}$ for $Q_y$ modes will be HT active, all of the vibrational modes that contain out-of-plane motions could also become HT active due to the break of the symmetry in the directions in the molecular plane. In total, there are 35 modes ($8 \, A_u, \, 8 \, B_{3g}, \, 9 \, B_{2g}$ and $10 \, B_{1u}$) that have HT activity for the TEFE process.

**S1.3 Allowed vibrational transition in the TEFE signal**

Because only 35 modes are HT active, we will have only 35 fundamental $0 \rightarrow 1'$ transitions in the TEFE spectra. Within the linear coupling model, where vibrational frequency changes as well as mode-mixing effect caused by the electronic transitions were neglected, the multi-dimensional vibrational wavefunctions ($|v_n\rangle$ and $|v_{n'}\rangle$) can be written as the direct product of corresponding single-mode vibrational wavefunctions as

$$|v_n\rangle = |n_1, n_2, n_3, \ldots n_N\rangle = \prod_{k=1}^{N} |n_k\rangle,$$

and

$$|v_{n'}\rangle = |n'_1, n'_2, n'_3, \ldots n'_N\rangle = \prod_{k=1}^{N} |n'_k\rangle.$$

Here $N$ is the total number of modes.

The transition matrix element for the fundamental HT transitions then reads

$$\mu_{i,0\rightarrow f, \nu_{HT}} = \sum_{HT} H_{i\rightarrow f, Q_{HT}} \langle 0_{HT}|Q_{HT}|1'_{HT}\rangle \prod_{l \neq HT} \langle 0_l|0'_l\rangle. \quad (S2)$$

Here we used the subscript of HT to represent the HT active modes in the TEFE process.

Considering the fact that none of these HT active modes are totally symmetric, both the vibrational integrals $\langle 0_l | 1'_{l'}\rangle$ and $\langle 0_l | Q_{l} | 0'_l\rangle$ will be 0 for these modes. As a result, only one term in the summation of Eq. S2 will be non zero. So that we have the transition matrix
element for the fundamental transition of the $h$-th mode as

$$
\mu_{i,0 \rightarrow f, \nu'_{HT}} = \mu_{i \rightarrow f, Q_{HT}}^{\nu'} \langle 0_{HT} | Q_{HT} | 1'_{HT} \rangle \prod_{l \neq HT} \langle 0_l | 0'_l \rangle. \quad (S3)
$$

Similarly, because both $\langle 0_l | 2'_{l} \rangle$ and $\langle 0_l | Q_l | 2'_{l} \rangle$ are 0 within the harmonic approximation, the overtone transitions for the HT active modes will be 0. As a result, $0 \rightarrow 2'$ overtone transitions of these HT active modes will have no contribution to the TEFE signal. The combination transitions consisting two HT active modes are also forbidden due to the same argument. This leave the combination transition consisting a HT active mode and a FC active mode as the only possible type of $0 \rightarrow 2'$ transitions in the TEFE signal.

Also due to the fact that $\langle 0_l | 1'_{l} \rangle = 0$ for the non-totally symmetric HT active modes and the dipole derivatives are 0 in the considered direction for the FC active modes, only one term in the summation of Eq. S2 will not be 0. We can get the following expression for the combinational transition consisting one HT active mode and the one FC active mode as

$$
\mu_{i,0 \rightarrow f, \nu'_{HT} \nu'_{FC}} = \mu_{i \rightarrow f, Q_{HT}}^{\nu'} \langle 0_{HT} | Q_{HT} | 1'_{HT} \rangle \langle 0_{FC} | 1'_{FC} \rangle \prod_{l \neq HT, FC} \langle 0_l | 0'_l \rangle. \quad (S4)
$$
Relation between the TEFE images of the fundamental and combinational transitions involving the same HT active mode

By comparing Eq. S3 and Eq. S4 we can find that the fundamental transition and the combinational transition differs with each other only by the FC integral, and both contain the same vibronic coupling term which determines the spatial distribution of the corresponding TEFE images. This explains the same patterns we obtained for the two types of transitions.

From Eq. S3 and Eq. S4 we can also obtain the cross section ratio between the fundamental transition and the combination transition involving the same HT active mode as

$$\frac{\sigma_{0\rightarrow1_{HT}^{H}}}{\sigma_{0\rightarrow1_{HT}^{C}}} = \frac{|\langle0_{FC}|1_{FC}'\rangle|^2}{|\langle0_{FC}|0_{FC}'\rangle|^2}. $$ (S5)

Within the LCM model applied in the present work, we can obtain both vibrational integrals from the corresponding Huang-Rhys factor ($S_{FC}$) of the FC active mode as

$$|\langle0_{FC}|1_{FC}'\rangle|^2 = e^{-S_{FC}} S_{FC}, $$ (S6)

$$|\langle0_{FC}|0_{FC}'\rangle|^2 = e^{-S_{FC}}. $$ (S7)

It can be seen from Eq. S6 and Eq. S7 that the cross section ratio between the fundamental transition and the combination transition equals to

$$\frac{\sigma_{0\rightarrow1_{HT}^{H}1_{FC}}}{\sigma_{0\rightarrow1_{HT}^{C}}} = S_{FC}. $$ (S8)

This indicates that TEFE could be applied to measure the Huang-Rhys factors for FC active modes in different electronic states. It should be noted however that LCM is an approximated model which is more accurate for molecular systems where the Duschinsky
mode mixing effect and frequency changes between the involved electronic states are not so strong. As a result, this method will be more effective for rigid molecules where frequency changes and mode mixing effect are normally not very important.
S3  Effect of non-Kasha’s rule emissions on the TEFE images

In this section we discuss the possible influence of the breakdown of Kasha’s rule on the results in the presented work. Breakdown of Kasha’s rule can happen when emission from excited vibrational levels within one excited state takes place. Another possibility is when photon emission from higher excited electronic states, such as the $S_2$ state in the $Q_y$ band of $H_2P$, takes place. Among these two types of non-Kasha’s rule emissions, the latter is not expected to have significantly influences on the resulting TEFE images of the $H_2P$ molecule because the two bands are well separated by 0.4 eV such that the emission spectra of the two states will not have significant overlap with each other. On the other hand, the hot emission from excited vibrational levels within one excited electronic state could lead to emissions that coincide in energy with the Kasha’s rule allowed emissions from the ground vibrational level and thus could affect the resulting TEFE spectra and images.

In order to exam such an effect, we have performed calculations based on rate equation simulations to describe the TEFE process and considered the influence of strongly enhanced radiative decay rates on the resulting TEFE images. For the $H_2P$ molecule investigated in the present work, only the fundamental $0_{HT} \rightarrow 1'_{HT}$ transitions of the out-of-plane non-totally symmetric HT active modes and its combinational $0_{HT}0_{FC} \rightarrow 1'_{HT}1'_{FC}$ transitions with the totally symmetric FC modes are active in the TEFE process. Our calculations indicate that the fundamental transitions are much stronger than the combinational transitions and dominate the TEFE spectra. For the convenience of discussion, we consider only a single incident frequency that was on resonance with one of the most intense fundamental transitions in the simulations. In this case, only this single mode will be excited during the excitation process and the photon excitation and possible decay processes can be described by the 8-level model shown in Figure S1.

The molecule can be excited to the excited state by the incident laser as indicated by
Figure S1: A schematic drawing for the model used to simulate the emission spectra and TEFE image for a given incident frequency. Blue upward arrow indicates the excitation process. Red and green downward arrows indicate the photon emissions originated from the ground and excited vibrational energy levels. Dashed blue arrows represent the vibrational decay process.

the blue upward arrow. After the excitation, the molecule will undergo both radiative and non-radiative decays. Radiative decay can happen at any level (solid downward arrows) that was populated. It should be mentioned that the spontaneous emission profile from the vibrational levels in the excited state contains also transitions to vibrational levels other than the four levels that was included in the current model. In the simulations these transitions can be included by taking into account the entire emission profile from the corresponding vibrational level that can be simulated beforehand.

For the non-radiative decay, we considered only the intra-state vibrational decays $\gamma_{vib}$ and neglected the inter-state decay, since we are mainly interested in the breakdown of Kasha’s rule. The latter can be easily incorporated into the model and is not expected to affect the resulting images. In the simulations, we follow the classic work of Johansson et al. and assume the intra-state vibrational decay rate from a level with $n$ quanta to the level with $n - 1$ quanta as $n\gamma_{vib}$ with $\gamma_{vib}$ being a parameter of vibrational decay rate.$^3$

The rate-equations that govern the excitation and decay processes in our model can be
written as

\[
\begin{align*}
\frac{dP_0}{dt} &= \sum_{i=0}^{3'} \gamma_{rad,i \rightarrow 0} P_i + \gamma_{vib}^{(g)} P_1 - \gamma_{exe,0 \rightarrow 1'} P_0, \\
\frac{dP_1}{dt} &= \sum_{i=0}^{3'} \gamma_{rad,i \rightarrow 1} P_i + 2\gamma_{vib}^{(g)} P_2 - \gamma_{vib}^{(g)} P_1 - \gamma_{exe,1 \rightarrow 2'} P_1, \\
\frac{dP_2}{dt} &= \sum_{i=0}^{3'} \gamma_{rad,i \rightarrow 2} P_i + 3\gamma_{vib}^{(g)} P_3 - 2\gamma_{vib}^{(g)} P_2 - \gamma_{exe,2 \rightarrow 3'} P_2, \\
\frac{dP_3}{dt} &= \sum_{i=0}^{3'} \gamma_{rad,i \rightarrow 3} P_i - 3\gamma_{vib}^{(g)} P_3,
\end{align*}
\]

(S9)

\[
\begin{align*}
\frac{dP_0'}{dt} &= -\sum_{i=0}^{3} \gamma_{rad,0' \rightarrow i} P_0' + \gamma_{vib}^{(e)} P_1', \\
\frac{dP_1'}{dt} &= -\sum_{i=0}^{3} \gamma_{rad,1' \rightarrow i} P_1' - \gamma_{vib}^{(e)} P_{1'} + 2\gamma_{vib}^{(e)} P_{2'} + \gamma_{exe,0 \rightarrow 1'} P_0, \\
\frac{dP_2'}{dt} &= -\sum_{i=0}^{3} \gamma_{rad,2' \rightarrow i} P_{2'} - 2\gamma_{vib}^{(e)} P_{2'} + 3\gamma_{vib}^{(e)} P_{3'} + \gamma_{exe,1 \rightarrow 2'} P_1, \\
\frac{dP_3'}{dt} &= -\sum_{i=0}^{3} \gamma_{rad,3' \rightarrow i} P_{3'} - 3\gamma_{vib}^{(e)} P_{3'} + \gamma_{exe,2 \rightarrow 3'} P_2.
\end{align*}
\]

Here \(P_i\) (\(P_{i'}\)) is the population of level \(i\) (\(i'\)) in the ground (first excited) state, \(\gamma_{exe}\) and \(\gamma_{rad}\) are the excitation and radiative decay rates, respectively. \(\gamma_{rad}^{g}\) and \(\gamma_{vib}^{(e)}\) represent the vibrational decay rates in the ground and excited state, respectively. By solving the rate equations to obtain the steady state population \(P^{ss}\), we can obtain the fluorescence signal of the system as

\[
I(\omega) = \sum_{i=0}^{3} \gamma_{rad} P_{i}^{ss} I_{i' \rightarrow n}(\omega).
\]

(S10)

Here \(I_{i' \rightarrow n}(\omega)\) is the emission profile from level \(i'\) in the excited state to the ground state. \(\gamma_{rad}\) is the total radiative decay rate from level \(i'\) to the ground state including the plasmonic enhancement.

As can be found from Figure S1 and Eq S10, Kasha’s rule can breakdown if the radiative decay rates become comparable or faster than the intra-state vibrational decay rates. In a nanocavity, the radiative decay rate is expected to be enhanced (via the Purcell effect) which could then lead to hot-luminescence that violates Kasha’s rule. For the model shown in Figure S1, the non-Kasha’s rule emission will mainly originate from the first excited vibrational
level 1′ because the other higher levels are not expected to be significantly populated. The emission profiles of the ground and first excited vibrational levels can be written as

\[ I_{0'\rightarrow n}(\omega) = \sum_n |\langle 0' | \hat{\mu} | n \rangle|^2 L(\omega_{0'n} - \omega), \]  
(S11)

\[ I_{1'\rightarrow n}(\omega) = \sum_n |\langle 1' | \hat{\mu} | n \rangle|^2 L(\omega_{1'n} - \omega), \]  
(S12)

with

\[ \langle 0' | \hat{\mu} | n \rangle = \mu_0 \langle 0' | n_A \rangle \prod_{k \neq A} \langle 0'_k | n_k \rangle + \frac{\partial \mu}{\partial Q_A} \langle 0'_A | Q_A | n_A \rangle \prod_{k \neq A} \langle 0'_k | n_k \rangle \]  
(S13)

\[ + \sum_{k \neq A} \frac{\partial \mu}{\partial Q_k} \langle 0'_k | Q_k | n_k \rangle \langle 0'_A | n_A \rangle \prod_{l \neq k, A} \langle 0'_l | n_l \rangle, \]

\[ \langle 1' | \hat{\mu} | n \rangle = \mu_0 \langle 1'_A | n_A \rangle \prod_{k \neq A} \langle 0'_k | n_k \rangle + \frac{\partial \mu}{\partial Q_A} \langle 1'_A | Q_A | n_A \rangle \prod_{k \neq A} \langle 0'_k | n_k \rangle \]  
(S14)

\[ + \sum_{k \neq A} \frac{\partial \mu}{\partial Q_k} \langle 0'_k | Q_k | n_k \rangle \langle 1'_A | n_A \rangle \prod_{l \neq k, A} \langle 0'_l | n_l \rangle. \]

Here we use the subscript A to represent the mode that could be involved in the hot-luminescence process as shown in Figure S1. Notice that all of the possible transitions from the corresponding level in the excited state to the ground state were included in the above equations for the emission profiles.

For the H$_2$P molecule, the vibrational modes that can be involved in the hot-luminescence process are non-totally symmetric HT active mode. As a result, the first and third terms to the right hand side of Eqs. S13 and S14 actually gives exactly the same line profile because we have \( \langle 0'_A | n_A \rangle = \delta_{0n_A} \) and \( \langle 1'_A | n_A \rangle = \delta_{1n_A} \). In this case, the difference between the emission profiles of level 0′ and 1′ will be caused solely by the second term in Eqs. S13 and S14. Our numerical calculations indicates that, for the non-totally symmetric out-of-plane modes that are active in the TEFE process of H$_2$P, the contribution of such term is negligible due to the small vibronic couplings (\( \frac{\partial \mu}{\partial Q_{HT}} \)). As a result, the emission profiles of the two levels
should be essentially the same for the H$_2$P molecule studied in the present work. This has been confirmed by the simulated emission profiles as shown in Figure S2(a-c). An important consequence for such an interesting feature is that the fluorescence spectrum will not change its profile even when the emission does not follow Kasha’s rule. As a result, as we will show by the following numerical calculations, the TEFE images for a given transition will also remain the same as that was obtained under the assumption of Kasha’s rule.

![Emission Profiles](image)

Figure S2: Emission profiles for the HT active mode $v_{45}$ (a-c) and the FC active mode $v_{13}$ (d-f) of H$_2$P molecule. (a) and (d) are Kasha’s rule emissions from the ground vibrational level $0'$ in the first excited state. (b) and (e) are non-Kasha’s rule emissions from the first excited vibrational levels $1'$. (c) and (f) show the differences between the emission profiles from the Kasha’s rule and non-Kasha’s rule emissions. The bar spectrum was broadened by Lorentzian functions with FWHM of 0.5 meV.

In the rate-equation simulations, we have set the incident frequency to be on resonance with the $0 \rightarrow 1'$ transition of mode $v_{45}$ in the $Q_x$ band with energy of 2.09 eV. The incident intensity was 100 W/cm$^2$, a plasmonic enhancement of $2.0 \times 10^5$ to the excitation rate has also been considered. The vibrational decay rates in the ground and excited states were assumed to be the same with a lifetime of 1.8 ps. The radiative decay rate was calculated from the lifetime of the $Q_x$ state which has been shown to be 10.7 ns in a nondegassed benzene.
Plasmonic enhancement to the radiative decay rates was artificially included with enhancement factors from 1 to $10^6$. The vibrational transition matrix elements were calculated based on our first-principles results.

Figure S3: TEFE images simulated with different radiative enhancement factors. Top row: TEFE images simulated from Eq. S10. Middle row: TEFE images simulated solely from the $0' \rightarrow n$ transitions. Bottom row: TEFE images simulated from the $1' \rightarrow n$ transitions.

Figure S3 shows the TEFE images obtained with the rate equation simulations with different enhancement factors to the radiative decay rate. From left to right, the enhancement factor has been set to 1.0, 100.0, 10 000.0 and 1 000 000.0, respectively. As clearly demonstrated by Figure S3, the TEFE images are dominated by emissions from the ground vibrational level ($0'$) when the radiative enhancement is small. The contribution from the hot non-Kasha’s rule $1' \rightarrow n$ transitions starts to gradually increase with the artificial increase of the plasmonic enhancement. At the enhancement around 10 000.0, which is sufficient to
balance the radiative \((0.93 \times 10^8 \text{ s}^{-1})\) and vibrational decay \((0.56 \times 10^{12} \text{ s}^{-1})\) rates, the contributions from the two types of transitions are comparable to each other. By further increase the radiative enhancement factor, such as to \(1000000.0\), the TEFE will be dominated by the non-Kasha’s rule \(1' \rightarrow n\) transitions. These features are as expected due to the competition of the different decay channels.

A striking feature can be found from Figure S3, however, is that the pattern of the TEFE images is obviously not affected by the involvement of the non-Kasha’s rule emissions. Such a feature is as expected because \(1' \rightarrow n\) gives the same emission profile and carries the same vibronic coupling information as those of \(0' \rightarrow n\) for the HT modes that was active in the TEFE process. These results confirmed that, even if non-Kasha’s rule emissions are involved, the main features of the vibronic couplings in \(H_2P\) that was captured by the TEFE images as presented in the main text will not be significantly affected.

Nevertheless, it should be mentioned that the breakdown of Kasha’s rule could have more significant influences on the TEFE process when FC active modes are involved. In such cases, all three terms to the right hand side of Eqs. S13 and S14 can be different. Fortunately, as a result of the weak FC activity of the vibrational modes in \(H_2P\), the differences between the Kasha’s rule and non-Kasha’s rule emissions are still expected to be quite small even when such FC mode are involved. This is confirmed by our numerical simulations shown in Figure S2(d-f) where we calculated the Kasha’s rule and non-Kasha’s rule emissions from the most active FC mode \((v_{13}, \text{ with Huang-Rhys factor of } 0.147)\) of \(H_2P\). It can be found that the overall profile of the non-Kasha’s rule hot emissions still recover the main features of that from Kasha’s rule \(0' \rightarrow n\) emissions very well. These results indicates that the possible involvement of FC active modes in the TEFE process is also not expected to have dramatic influences on the resulting images of \(H_2P\).

For more general cases of molecules in plasmonic nanocavity, the FC contributions would be much significant. To better understand the influence of the non-Kasha’s rule emissions involving the FC active mode, we have also performed calculations where we artificially in-
Figure S4: Emission profile of the Kasha’s rule $0' \rightarrow n$ transitions and non-Kasha’s rule $1' \rightarrow n$ transition for the FC active mode $v_{13}$ of $\text{H}_2\text{P}$ molecule with artificially increased FC activity.

Increased the FC activity of $v_{13}$ in $\text{H}_2\text{P}$ by 3 times which will give us a Huang-Rhys factor of 0.441. The obtained emission profiles for the Kasha’s rule emission and the non-Kasha’s rule hot emissions are shown in Figure S4. It can be clearly seen that, in this case, not only the high energy emissions take place in the non-Kasha’s rule emission but also the whole emission profiles are significantly different between the non-Kasha’s and Kasha’s emissions. Such strong changes to the luminescence profiles caused by the non-Kasha’s rule emissions can have significant influences on the proposed TEFE process which measures the wavelength dependent intensity changes to the fluorescence spectra. Experimentally, the possible emergence of such a problem can be checked by comparing the fluorescence spectra obtained with different incident frequencies. A change of the emission profile indicates that the Franck-Condon active modes could be involved for the non-Kasha’s rule luminescence process and the interpretation of the resulting TEFE spectra and images should take such non-Kasha’s rule features into account.
We would like to note that the above mentioned FC transitions are forbidden in the optically excited TEFE process for the model considered in the present work, where we are focused on the vibronic effect associated with HT active modes. Thus, the interesting features of the optically excited luminescence process from the allowed HT modes justify that the main results reported in the main text, i.e., the distinct imaging patterns of different HT active modes will not be affected even when Kasha’s rule breaks down.
Field distribution of $E_{\text{eff}}$

As mentioned in the main text, in the present work, we set $R_0$ as the center of the plasmonic field. We can further assume that the normalized $E$ exponentially decays from the plasmonic center, i.e.,

$$E = e^{-\kappa r},$$

(S15)

where $\kappa$ is the decay rate. According to the definition (Eq. 4 and related discussion in the main text), we have

$$E_{\text{eff}} = \int_0^1 e^{-\lambda \kappa r} d\lambda = 1 - e^{-\kappa r}$$

(S16)

![Figure S5: Calculated $E_{\text{eff}}$ by Eq. S16 (black line) and the fitting by Gaussian functions (red line).](image)

Schematic illustration of $E_{\text{eff}}$ was depicted in Figure S5 (black line), which also decays from the plasmonic center. As a result, $E_{\text{eff}}$ can be fitted very well by some Gaussian
functions (red line) as shown in Figure S5.

S5 Transformation formula for TEFE images

From Eq. 7 in the main text, we can obtain the TEFE spectra as

$$I(\omega, R_T) = A \sum_{i,n;f,n'} \rho_{i,n} \left| \sum_k \mu_{i \rightarrow f,Q_k}^{e'f} \langle v_n | Q_k | v_{n'} \rangle \right|^2 L(E_{f,n'} - E_{i,n} - \hbar\omega),$$

(S17)

where $L(E_{f,n'} - E_{i,n} - \hbar\omega)$ is a line shape broadening function with $E_{f,n'}$, $E_{i,n}$ and $\hbar\omega$ being the energies for the final state, initial state and the incident photon, respectively. In practical calculations, we have used Lorentzian functions for the broadenings. $A$ is a constant pre-factor that takes into account possible field dependence of the spectra, $\rho_{i,n}$ is included to describe possible thermal distributions of the initial state at finite temperatures. At low temperatures such as considered in the main text, only the lowest vibrational level $i,0$ will be significantly populated. Since the transition dipole moment $\mu_{i \rightarrow f,Q_k}^{e'}$ is dependent on the tip position $R_T$, the TEFE image can be constructed with a fixed incident frequency $\omega$ at different tip positions.

S6 Influence of metallic tip on the absorption spectra of the molecule

We calculated the absorption spectra of the $\text{H}_2\text{P}$ molecule in the $Q_x$ band by taking into account the influence of a model silver tip described by an Ag$_{20}$ cluster, the results are shown in Figure S6. For all three tip positions considered, the spectra remain largely unchanged at distances larger than 0.4 nm. Only when the tip-molecule distance decreased to be smaller than 0.4 nm, we start to observe clear changes in the absorption profile, especially when the tip is not located above the center of the molecule. These results indicate that, for $\text{H}_2\text{P}$, the
Figure S6: Tip-molecule distance-dependent $Q_x$ band absorption spectra of the H$_2$P molecule. (a) Side view of the model used in the calculations. The tip was placed on top of (b) the center of the molecule, (c) the C atom in the methine group, (d) the N atom. The tip is not likely to have a significant influence on the electronic transition properties of the molecule for tip-molecule distances larger than 0.4 nm.
S7 Validation of the linear coupling model

Figure S7 shows the $z$ component of the absorption spectra in the $Q_x$ and $Q_y$ bands as calculated by taking into account both the frequency changes and Duschinsky rotation effect (exact calculation, black line) and by the linear coupling model (LCM, red line).

Figure S7: Comparison of the $z$ component of the absorption spectra in the $Q_x$ (a) and $Q_y$ (b) bands as calculated by the exact calculation (black line) and by the LCM (red line).
S8  Detailed analysis of the absorption spectrum of the H\textsubscript{2}P molecule in free space

Figure S8 shows the calculated absorption spectrum contains both Franck-Condon (FC) and Herzberg-Teller (HT) terms (red line), only FC term (blue line) and only HT term (green line) of the H\textsubscript{2}P molecule in free space together with the experimental spectrum measured in vapor phase (adopted from Ref. 8, red line). It can be immediately found that the HT term is the dominant contribution for both bands. On the contrary, the FC term only contributes to the 0-0 band near 1.98 eV and 2.42 eV for the $Q_x$ and $Q_y$ bands, respectively, which should be attributed to the small transition dipole moments of the two bands in H\textsubscript{2}P.

![Diagram showing the absorption spectrum comparison](image)

Figure S8: Comparison of the experimental spectrum (black line) and the calculated spectra. The red, blue, and green lines are obtained with FC and HT, FC, and HT terms, respectively. The spectra have been vertically shifted for comparison. The experimental spectrum was adapted from Ref. 8, with permission from Elsevier.
S9 Detailed assignment for the TEFE images

Due to the finite broadening of the TEFE spectra, the TEFE image obtained at a specific frequency may contain the contribution from nearby vibrational modes. In this section we make a detailed assignment for the TEFE images shown in Figure 2 of the main text. The assignment for the TEFE images of the $Q_y$ and $Q_x$ bands were shown in Figure S9 and Figure S10, respectively. In these two figures the images obtained from the broadened TEFE spectra were shown in the top panel. The images for individual vibrational modes constructed from the un-broadened bar spectra were shown in the lower panels.

Figure S9: Detailed analysis of the four images in the $Q_y$ band. Top panel shows the images obtained from the broadened TEFE spectra. The lower panels are the images obtained from the individual vibrational modes of the un-broadened bar spectra. All of the vibrational modes that could contribute to the images shown in the top panels have been included.
For the $Q_y$ band, three out of the four transitions ($0 \rightarrow 1'_2$, $0 \rightarrow 1'_{20}$ and $0 \rightarrow 1'_{45}$) are dominated by the mode on resonance with the transition. For the $0 \rightarrow 1'_{29}$ transition, the ring like pattern are contributed jointly by the two modes of $\nu_{29}$ and $\nu_{30}$. The high energy modes of $\nu_{31}$ and $\nu_{32}$ as well as several low energy transitions that are close in frequency also have some minor contributions to this image.

Figure S10: Detailed analysis of the four images in the $Q_x$ band. Top panel shows the images obtained from the broadened TEFE spectra. The lower panels are the images obtained from the individual vibrational modes of the un-broadened bar spectra. All of the vibrational modes that could contribute to the images shown in the top panels have been included.

From Figure S10 we can find that the $0 \rightarrow 1'_2$ transition is dominated by mode $\nu_1$, which is close in energy to the $0 \rightarrow 1'_2$ transition and has much larger TEFE cross section than mode $\nu_2$. $\nu_2$ plays a minor role due to the relative small cross section. For the $0 \rightarrow 1'_{20}$ transition, as can be found in Figure S10, the image is jointly determined by mode $\nu_{20}$ and $\nu_{21}$. The
combination of the bright lobes in these two images resulted in the bright and diffused lobes in the image obtained from the broadened spectra. Due to the near degeneracy of vibrational modes, the image for the $0 \rightarrow 1'_{29}$ transition contains the contributions of four modes with mode $\nu_{29}$ being the most important one. The image for the $0 \rightarrow 1'_{45}$ is relatively simple and is dominated by mode $\nu_{45}$.

**S10 Transition density of the two states**

(a) (b)

![Figure S11: Top view of the electronic transition density with isovalue of 0.003 for the $Q_y$ and $Q_x$ bands.](image)

**S11 Influence of the field confinement on the TEFE images**

Figures S12 (for the $Q_y$ band) and S13 (for the $Q_x$ band) depicted the TEFE images calculated with 2 Å (top), 5 Å (middle) and 8 Å (bottom) plasmonic fields. It can be found that the TEFE images obtained with a 2 Å field can nicely reflect detailed real space distributions of the vibronic couplings at the single-atomic level. The TEFE images become, as expected, more diffused when the larger plasmonic field was used. However, the main features in TEFE images with the 2 Å plasmonic field are almost all reserved with the more realistic plasmonic field.
Figure S12: TEFE images in the $Q_y$ band as simulated with different sized plasmonic fields. (a) $\alpha_x = \alpha_y = 2 \text{ Å}$, (b) $\alpha_x = \alpha_y = 5 \text{ Å}$, (c) $\alpha_x = \alpha_y = 8 \text{ Å}$.

Figure S13: TEFE images in the $Q_x$ band as simulated with different sized plasmonic fields. (a) $\alpha_x = \alpha_y = 2 \text{ Å}$, (b) $\alpha_x = \alpha_y = 5 \text{ Å}$, (c) $\alpha_x = \alpha_y = 8 \text{ Å}$.

**S12 Spatial resolution of the TEFE images**

In Figure S14, we give an analysis to the spatial resolution of the TEFE images as obtained with different sized plasmonic fields. For the SCP field with $\alpha_x = \alpha_y = 2 \text{ Å}$, the spatial resolution of the TEFE images is 1.7 Å, as shown in Figure S14. For the more realistic
sizes of 5 Å and 8 Å, the resolutions were estimated at 3.4 Å and 4.6 Å, respectively. These results indicate that the spatial resolution of the TEFE image is closely related to the spatial confinement of the SCP.

![Diagram of TEFE images](image-url)

Figure S14: Top: TEFE images for the $0 \rightarrow 1'_{45}$ transition in the $Q_x$ band as simulated with different plasmonic sizes of 2, 5, and 8 Å, from left to right. Bottom: The line profile along the dashed line in the top panel, which illustrates the spatial resolution of the images.
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