Supporting Information

for the article:

Two-Dimensional Electronic Spectroscopy of Anharmonic Molecular Potentials

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Contents

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List of Figures

Contributions from the Rephasing and Nonrephasing Terms to the Zero-Phonon Peak

The ZPPs in Fig 2 are constituted by the four terms R_1, R_2, R_3 and R_4. However, since R_1 and R_4 are equal, the sum of these are just plotted as the nonrephasing signal, and likewise for the rephasing terms R_2 and R_3. These contributions are plotted in Figure S1.

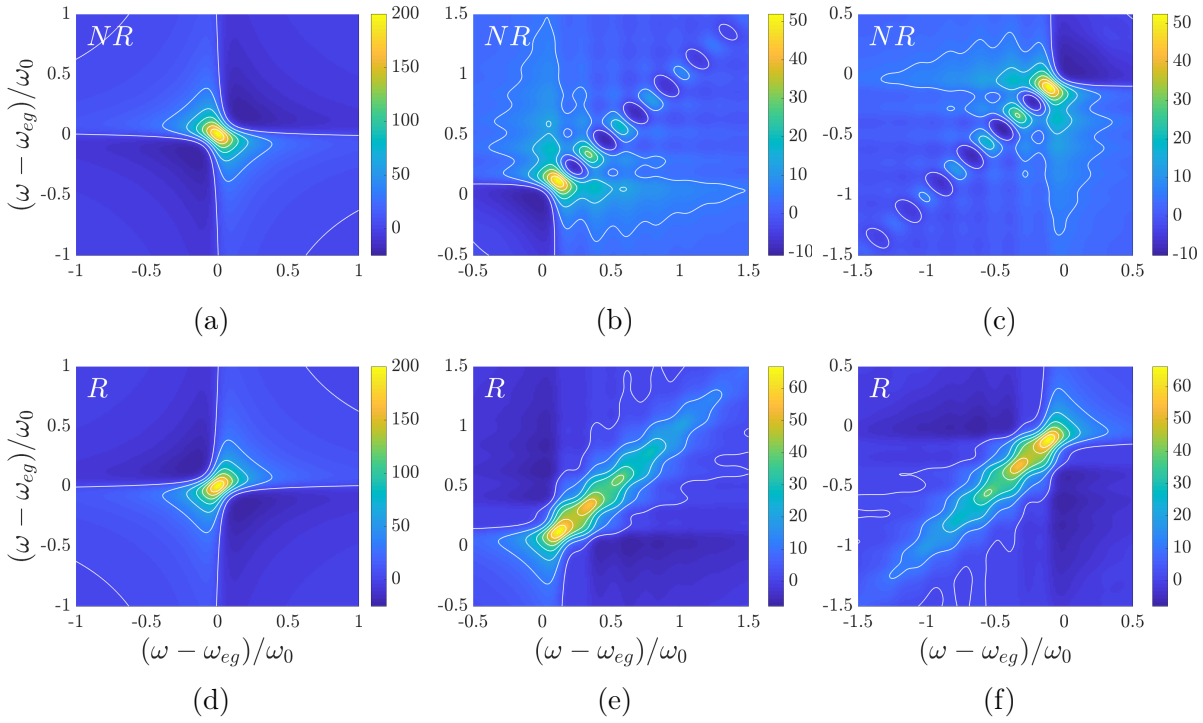

Figure S1: Nonrephasing (NR) and rephasing (R) spectra of undisplaced harmonic oscillators with ground state potential $V_g = 0.5x^2$ and excited state potential (a,d) $V_e = 0.5x^2$, (b,e) $V_e = 0.7x^2$ and (c,f) $V_e = 0.3x^2$. The NR terms, R_1 and R_4 are identical, and so are the R terms, R_2 and R_3.

Contributions from Individual Terms to the Infinite Waiting Time Spectra

By inspecting the individual contributions, or the rephasing and nonrephasing spectra, symmetries which are not present in the total absorptive spectra can be seen.

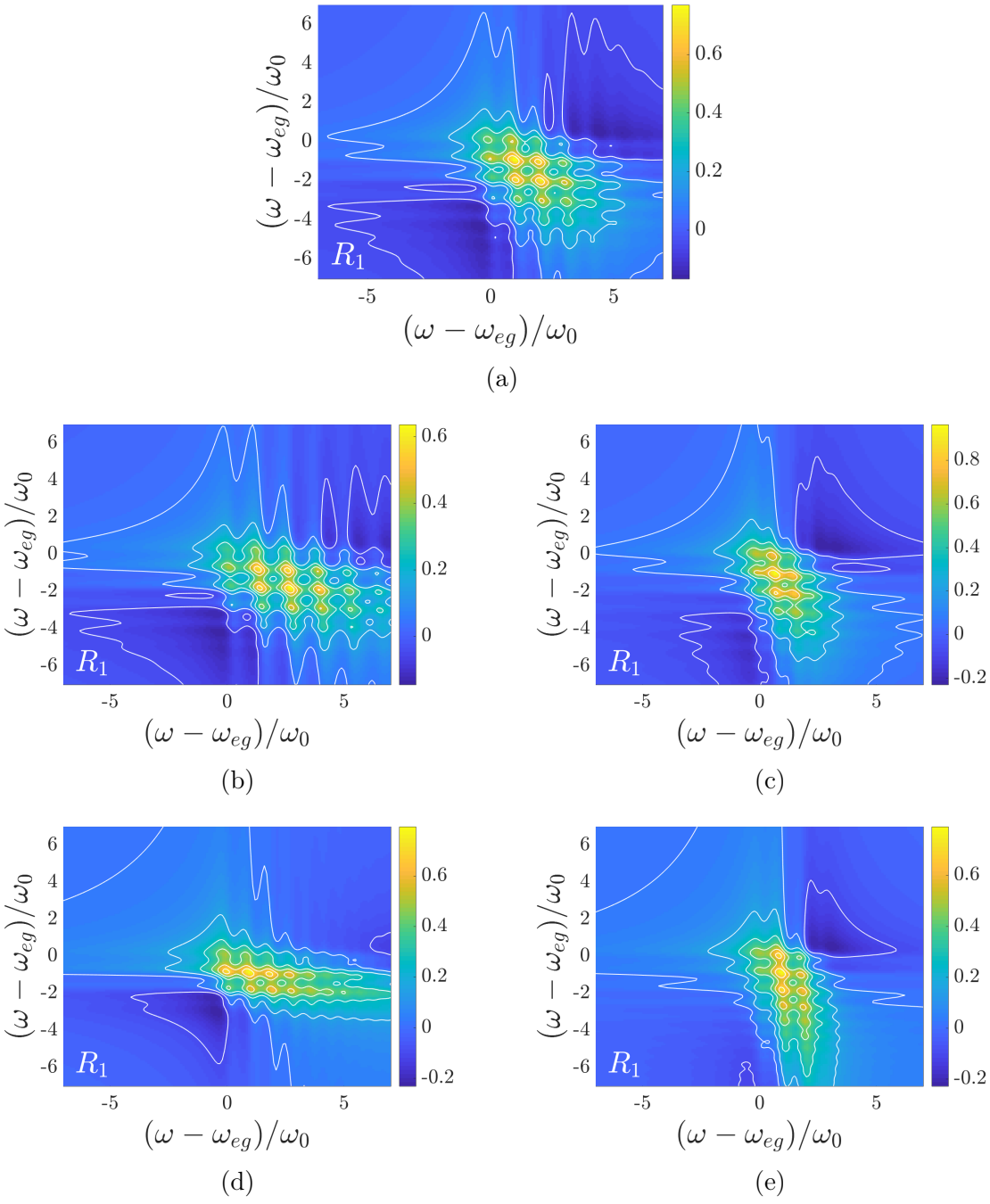

Figure S2: R1 contributions to the spectra in Fig 3.

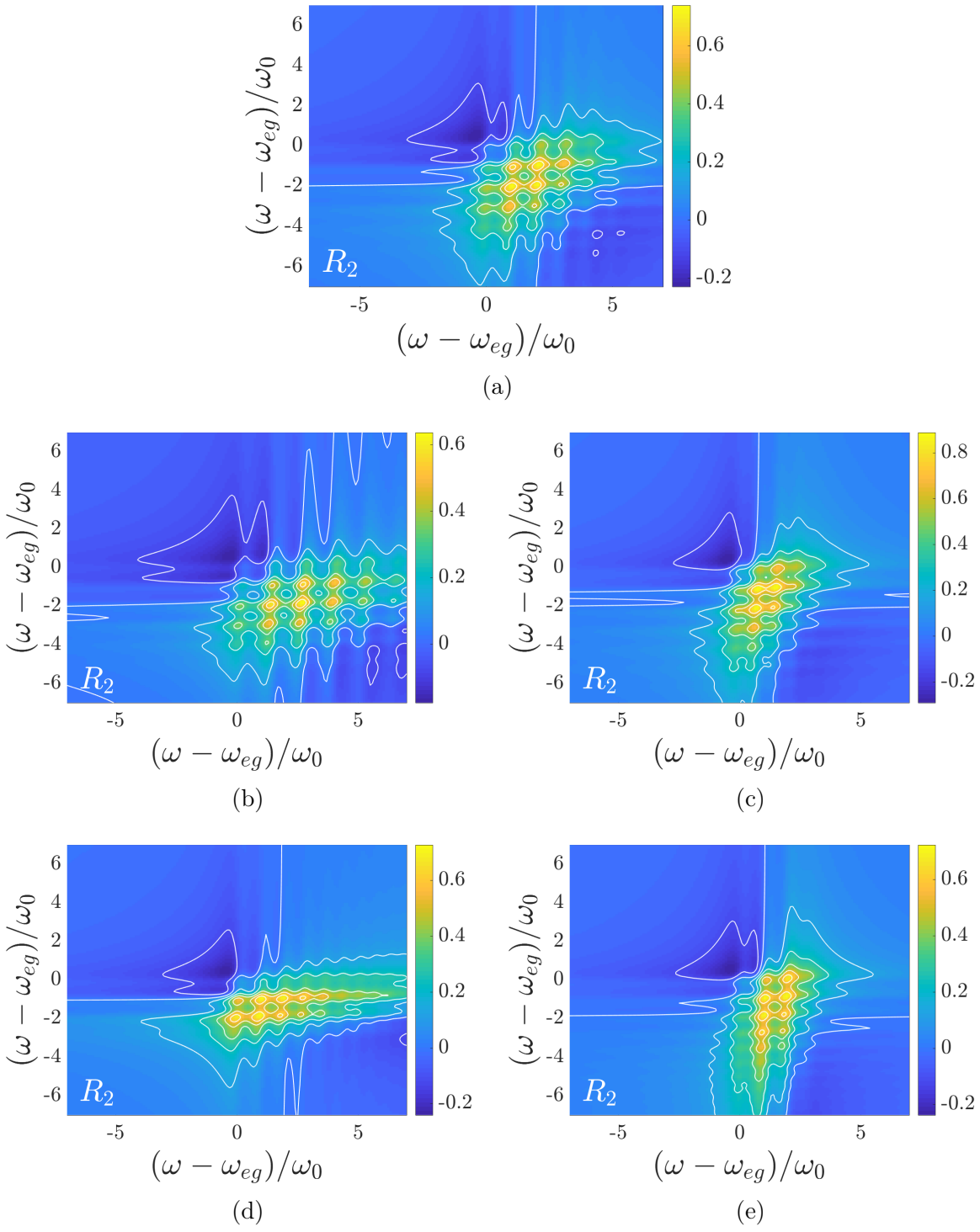

Figure S3: R2 contributions to the spectra in Fig 3.

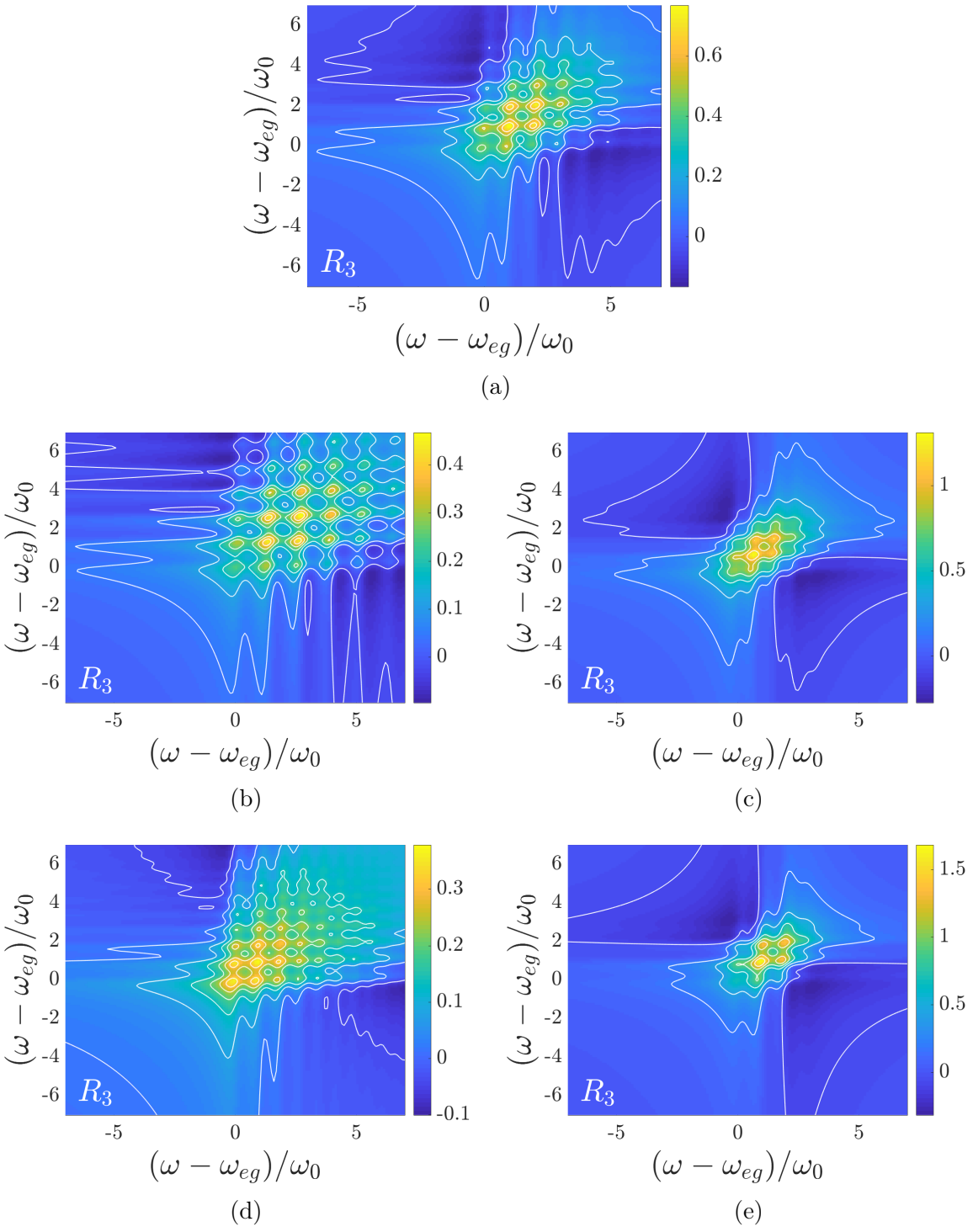

Figure S4: R3 contributions to the spectra in Fig 3. Note how the GSB signal is symmetric about the diagonal, regardless of which model system was used.

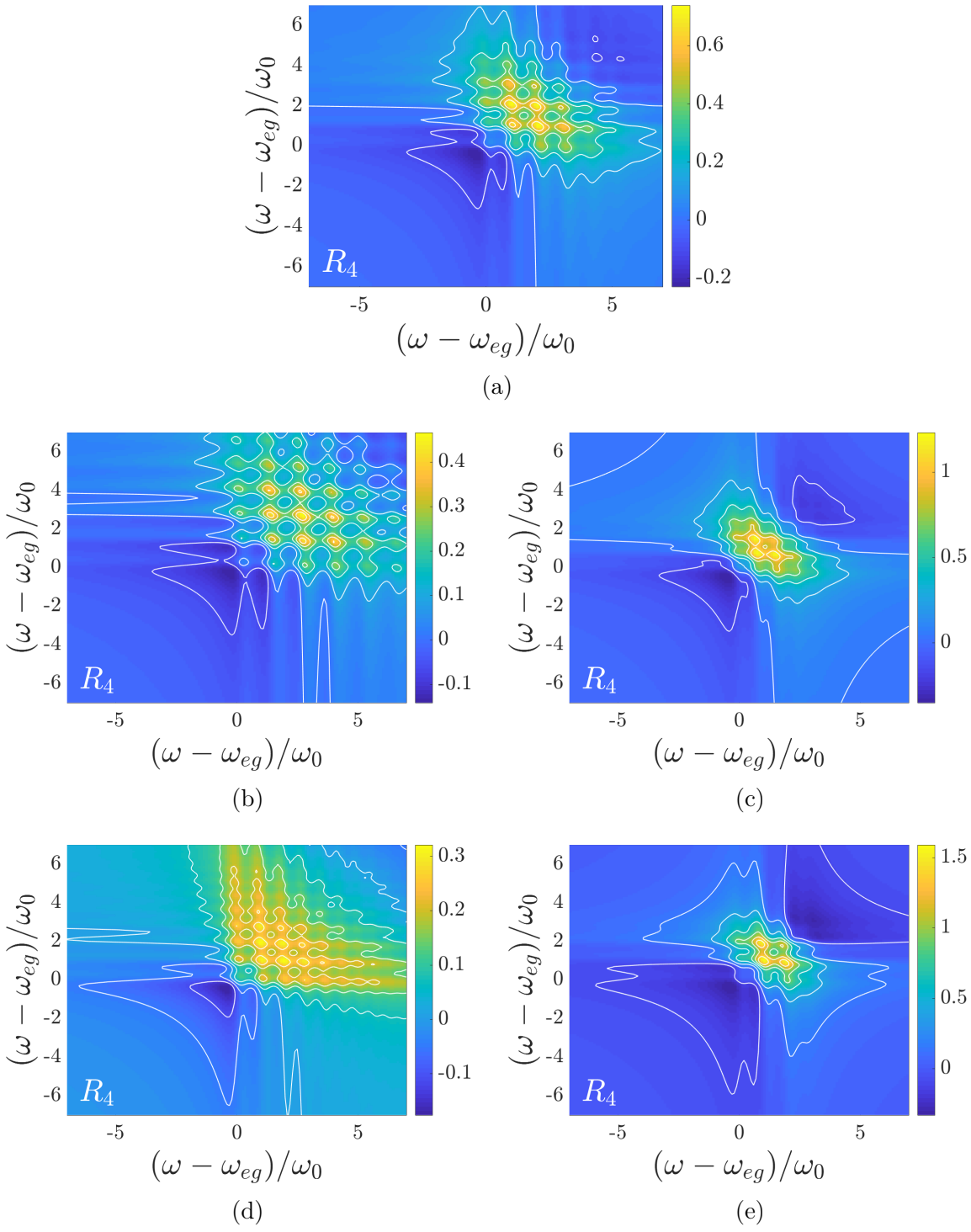

Figure S5: R4 contributions to the spectra in Fig 3. Note how the GSB signal is symmetric about the diagonal, regardless of which model system was used.

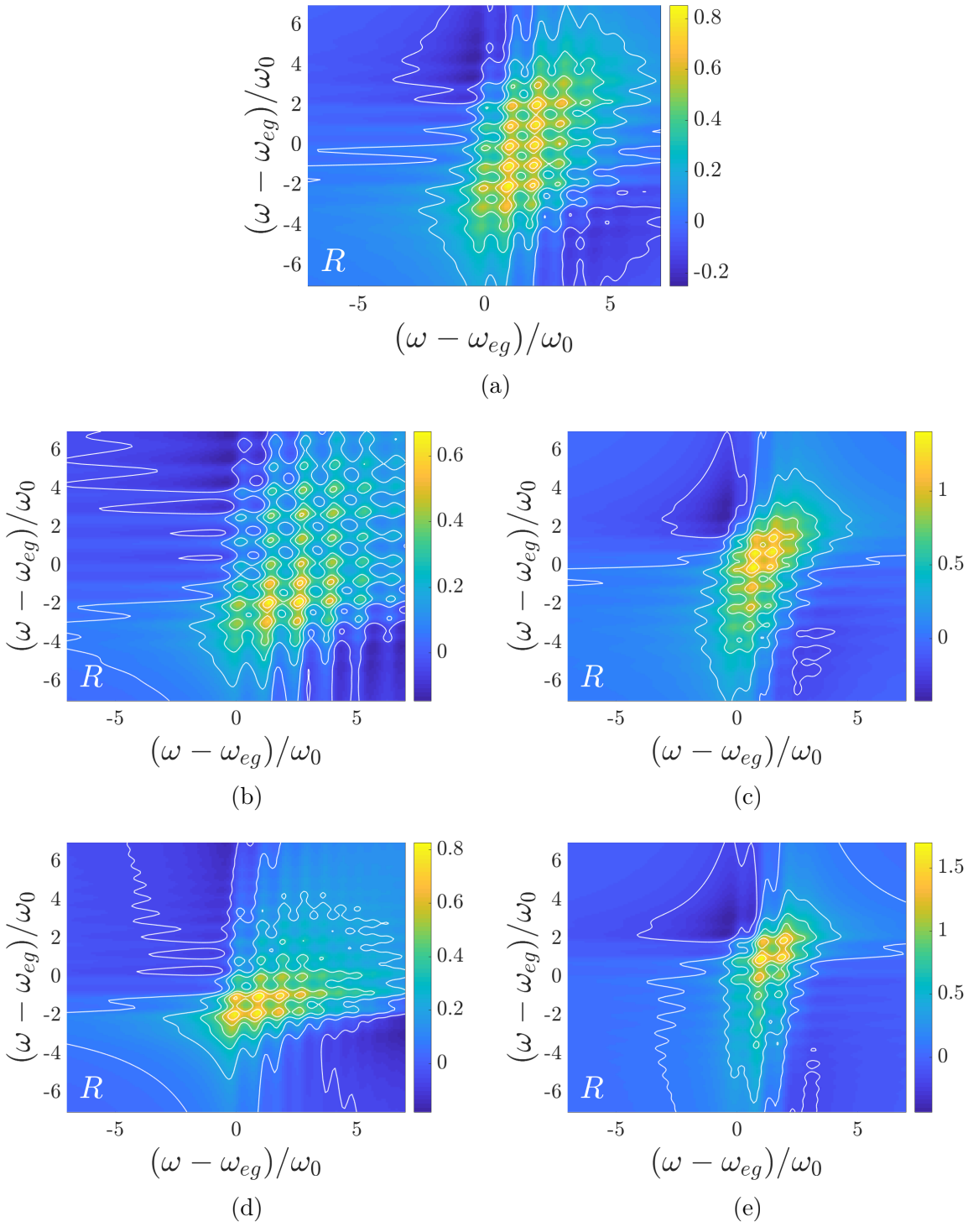

Figure S6: Rephasing contributions to the spectra in Fig 3.

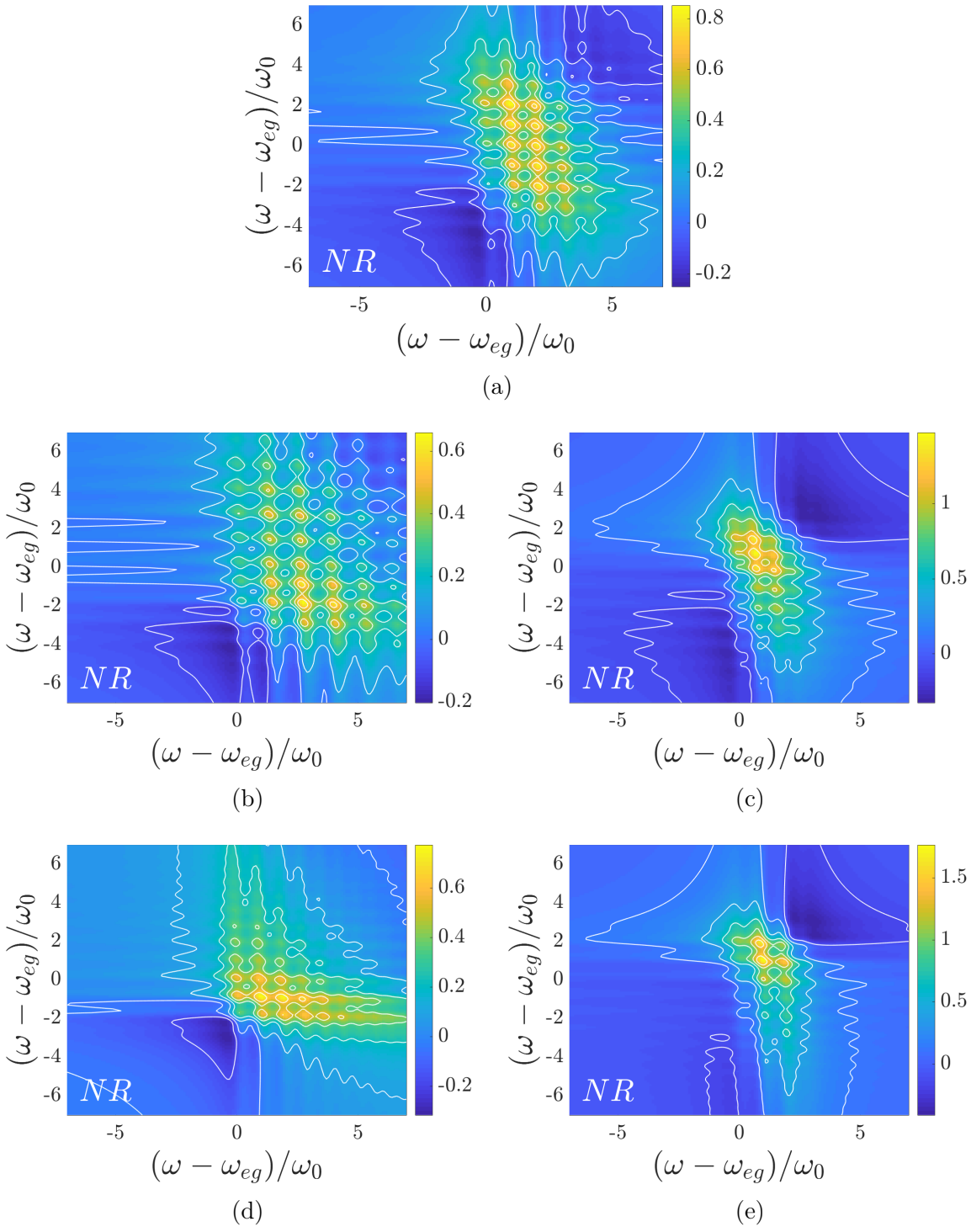

Figure S7: Nonrephasing contributions to the spectra in Fig 3.

Contributions from Individual Terms to the Short Waiting Times' Spectra

R1 Terms

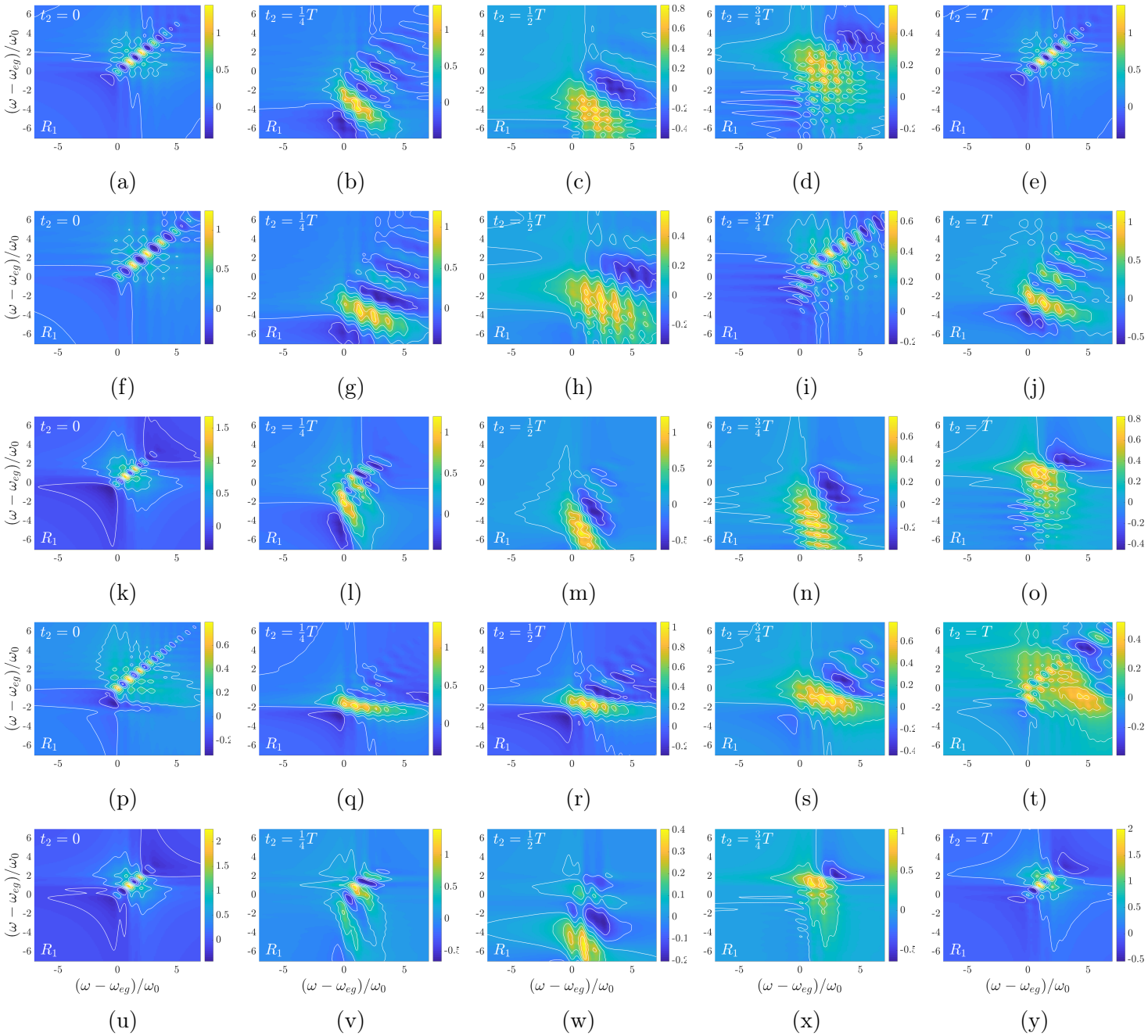

Figure S8: 2D spectra of the R_1 pathway of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

R2 Terms

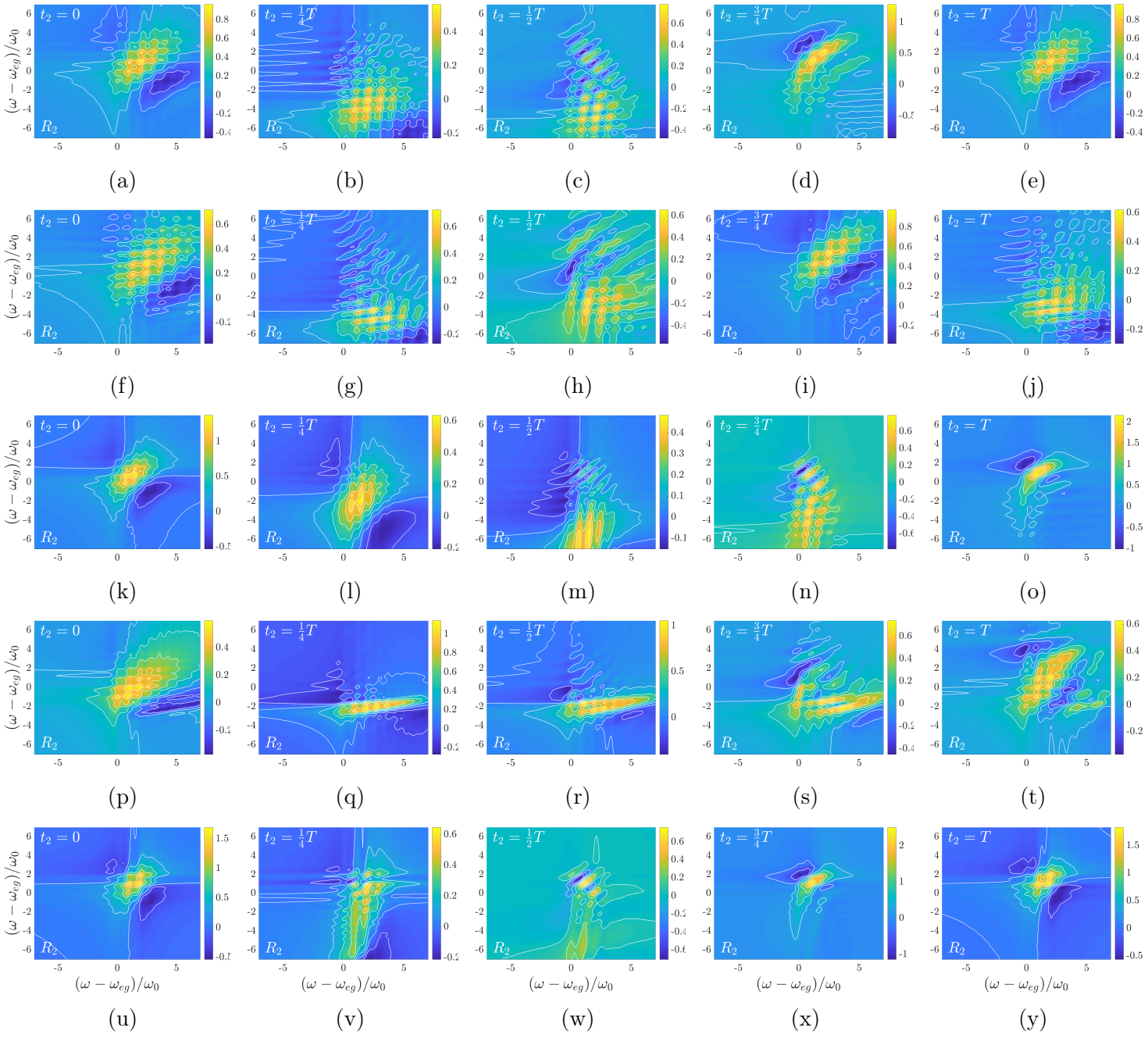

Figure S9: 2D spectra of the R_2 pathway of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

R3 Terms

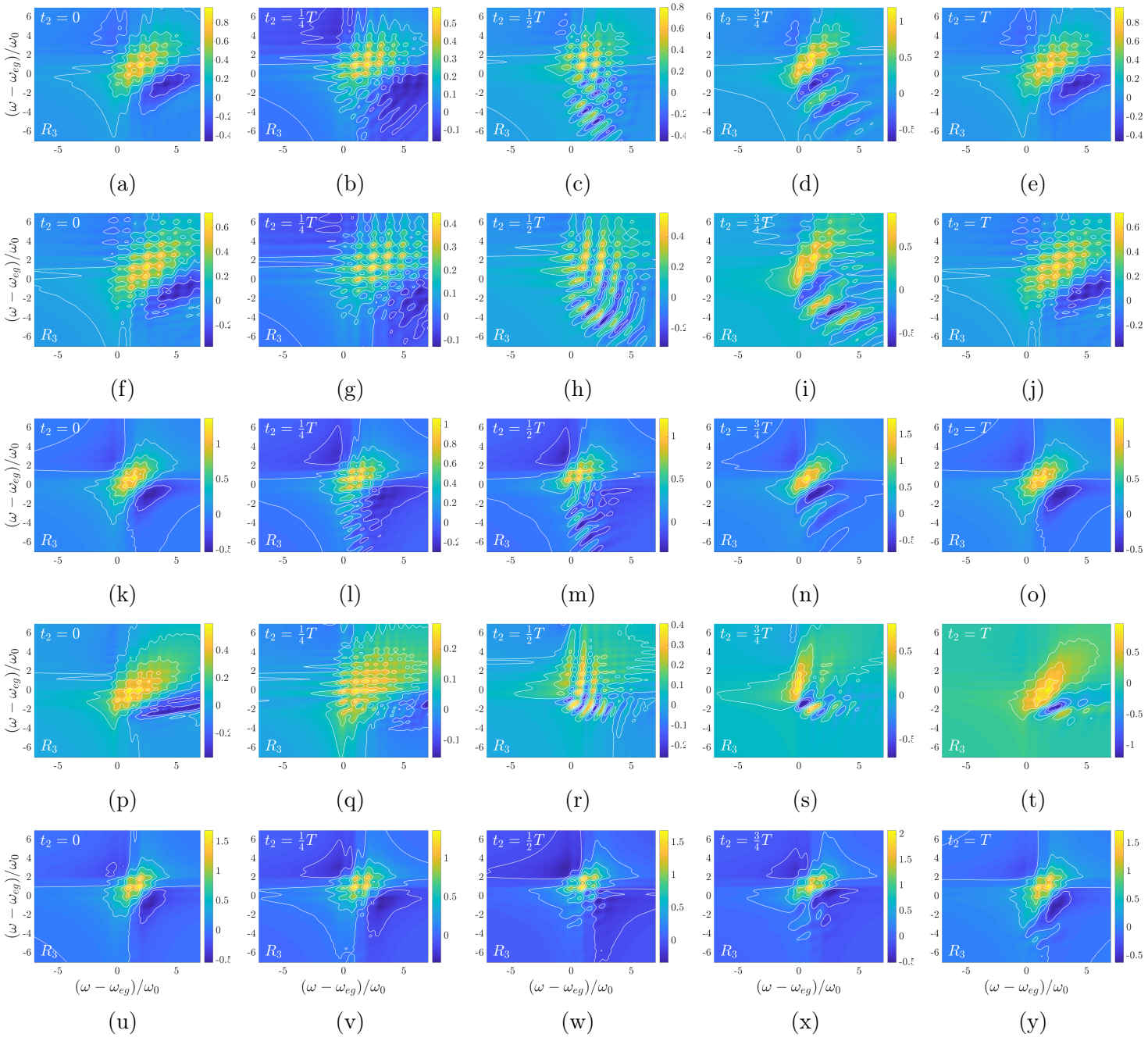

Figure S10: 2D spectra of the R_3 pathway of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

R4 Terms

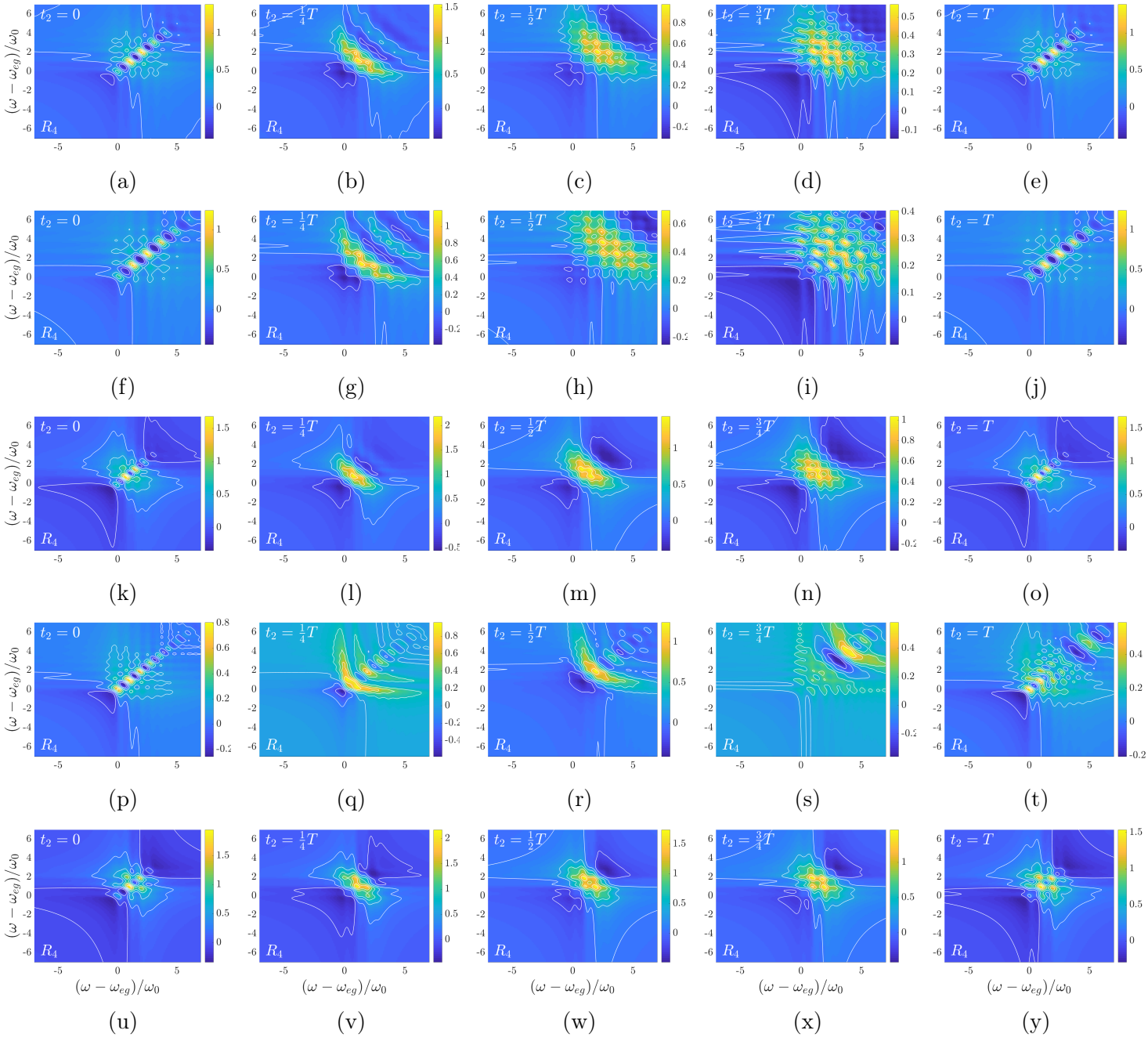

Figure S11: 2D spectra of the R_4 pathway of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

Rephasing Spectra

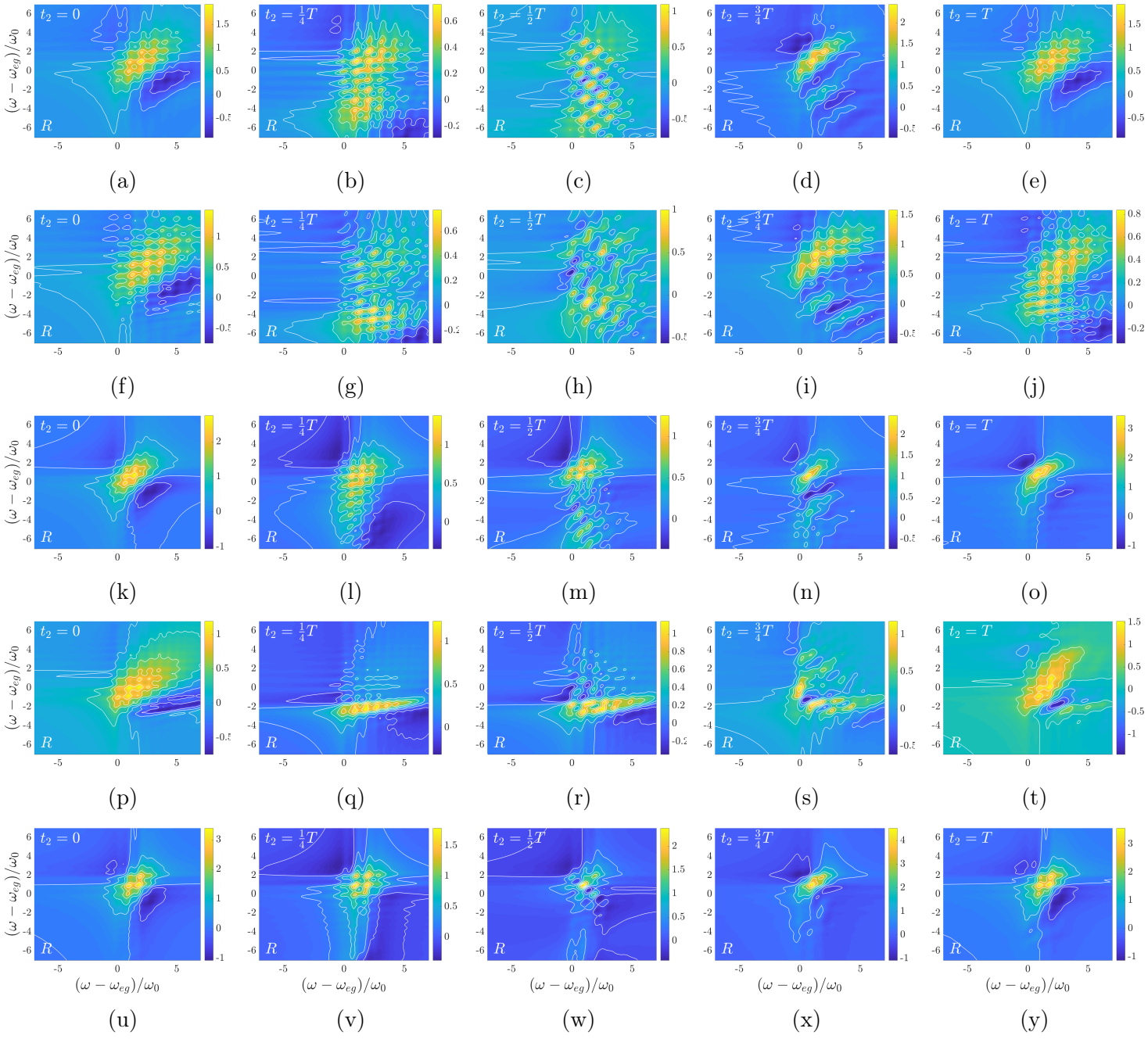

Figure S12: 2D spectra of the rephasing pathways of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

Nonrephasing Spectra

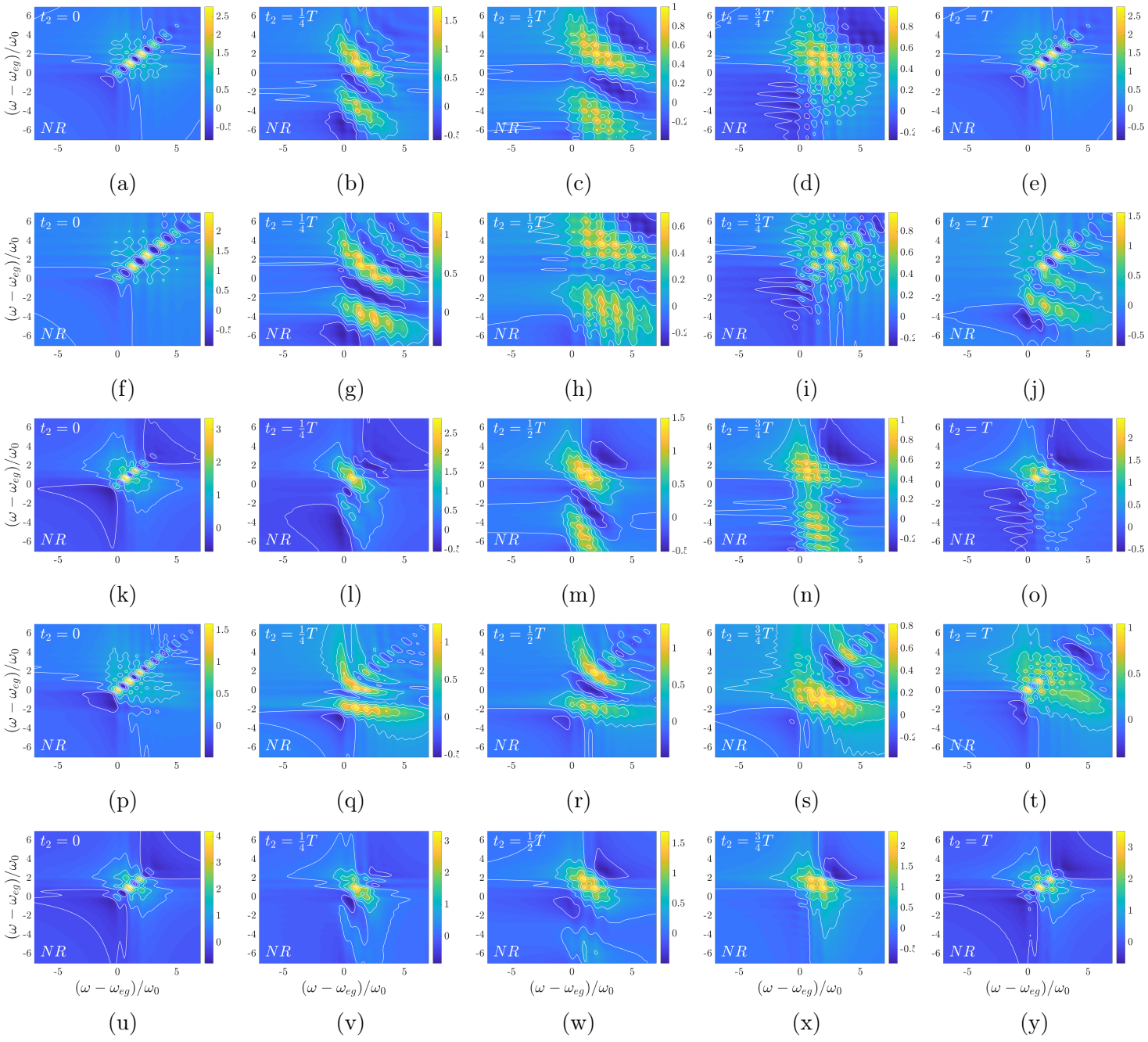

Figure S13: 2D spectra of the nonrephasing pathways of the displaced two-level systems we considered in the main text. Each row corresponds to the systems depicted on the left of Fig. 3. The waiting time corresponds to a fraction of the period T.

Effect of Stronger Dephasing

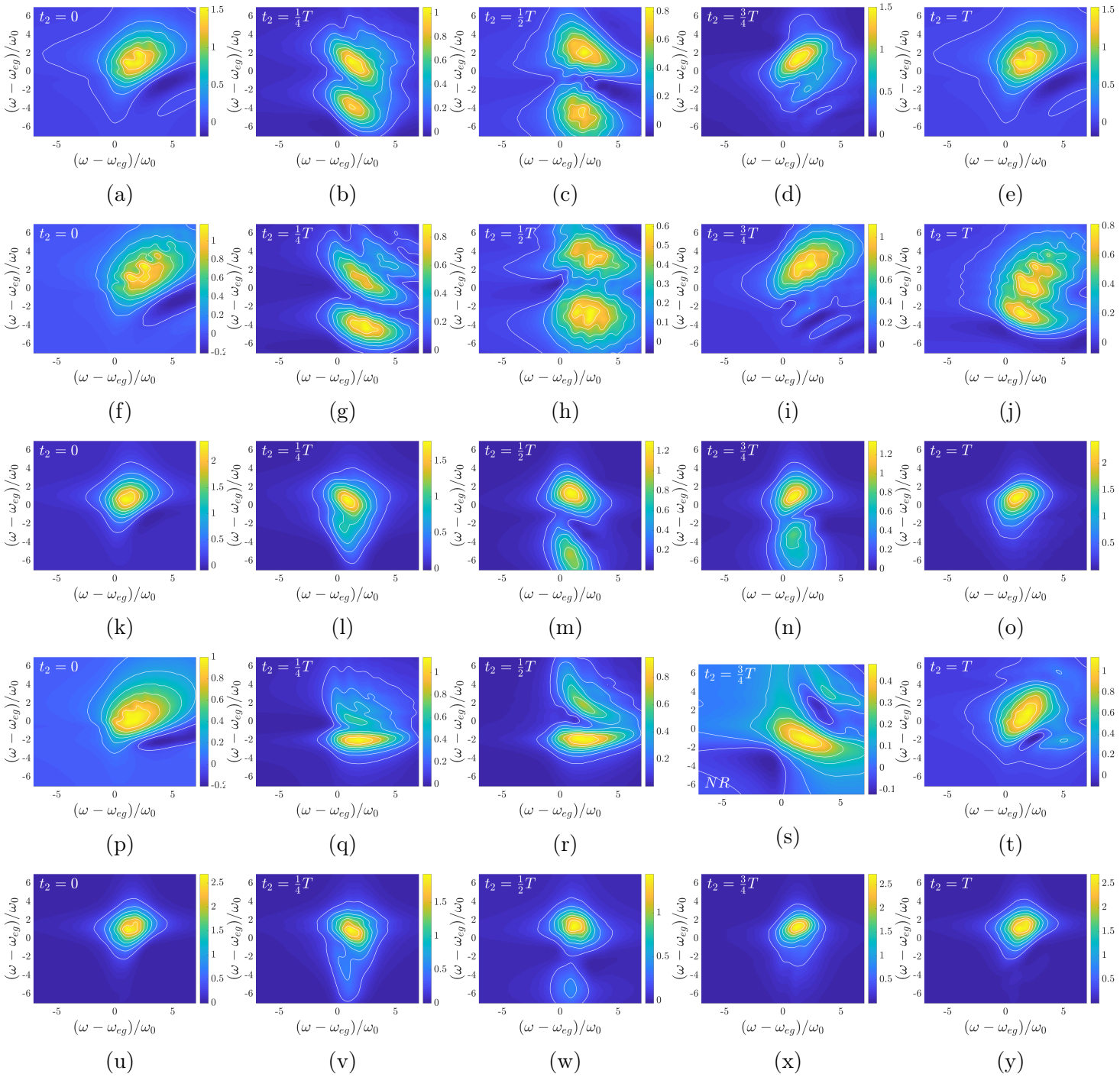

Figure S14: Total absorptive 2D spectra at short waiting times with double dephasing strength relative to Fig. 4 in the main text (now $\gamma = 0.8\omega_0$, and not $\gamma = 0.4\omega_0$). Each row corresponds to the systems depicted on the left of Fig. 3. The remaining parameters are identical to the main text case. The waiting time corresponds to a fraction of the period T.

Effect of Smaller Displacement

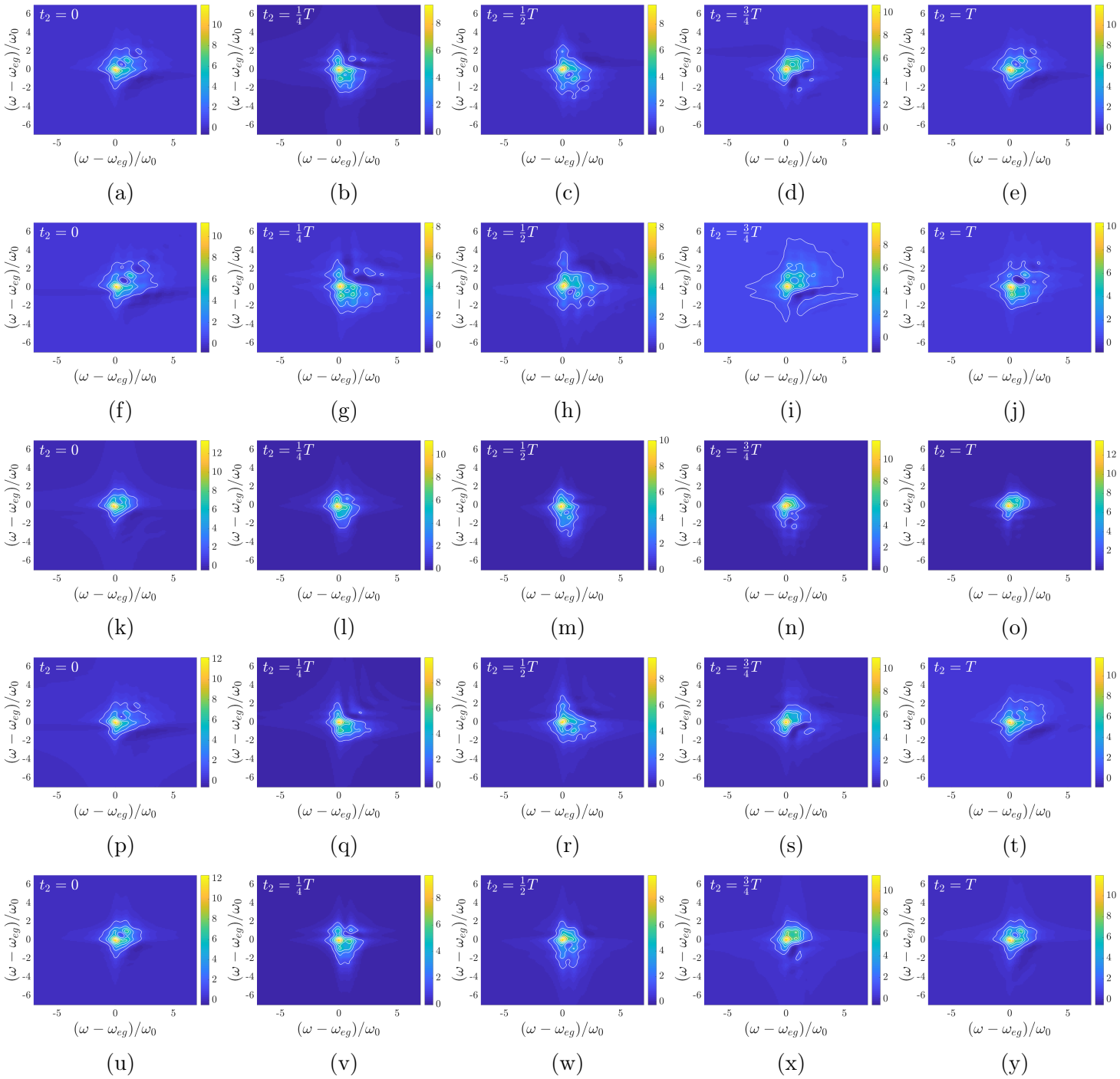

Figure S15: Total absorptive 2D spectra at short waiting times with smaller displacements relative to Fig. 4 in the main text (now $d = \pm 1$, and not $d = \pm 2$). Each row corresponds to the systems depicted on the left of Fig. 3. The remaining parameters are identical to the main text case. The waiting time corresponds to a fraction of the period T.

Effect of Smaller Anharmonicity

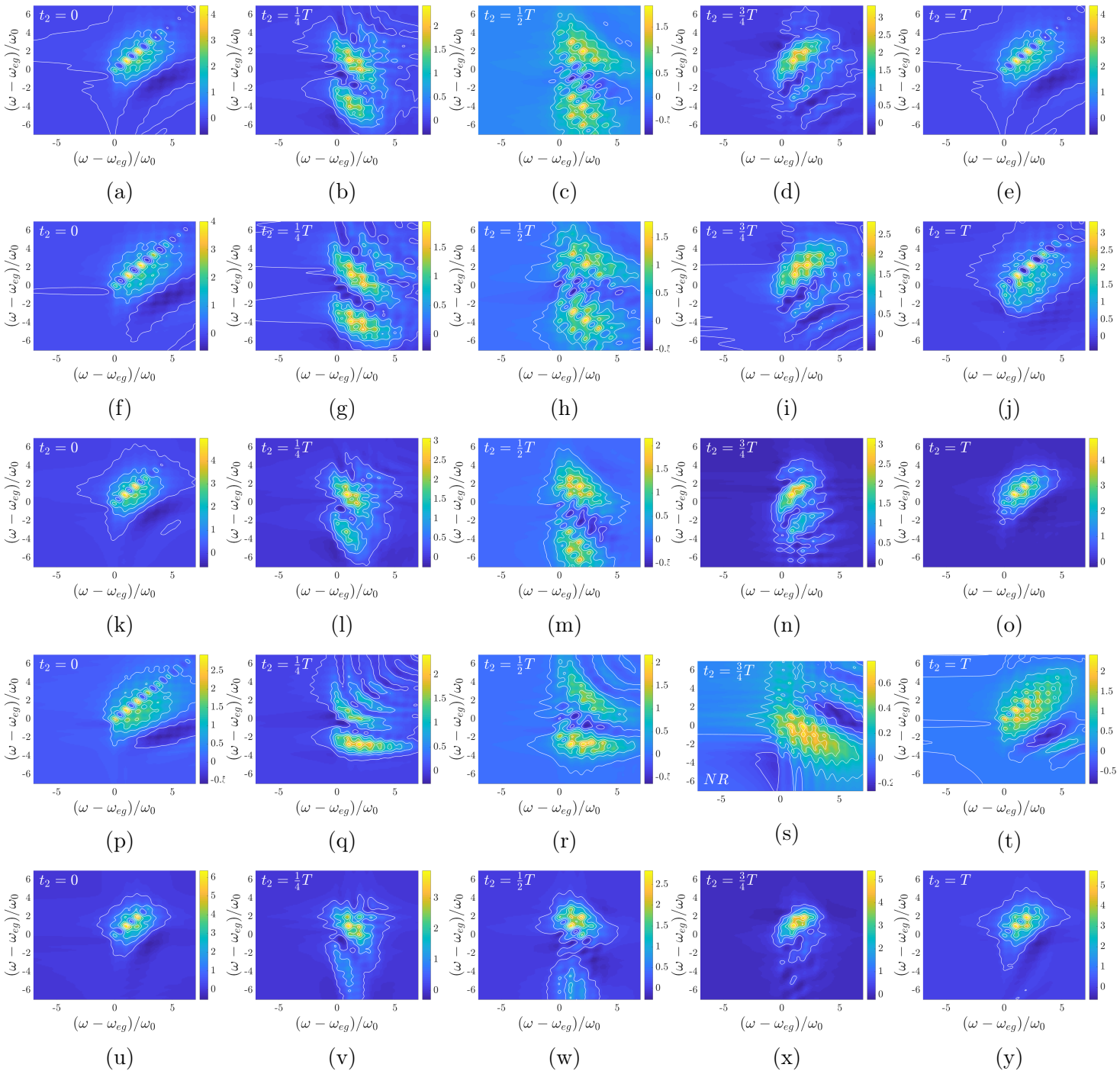

Figure S16: Total absorptive 2D spectra at short waiting times with smaller anharmonicities relative to Fig. 4 in the main text. The first row is the reference system of displaced harmonic oscillators with equal frequencies, hence it is identical to the upper row of the figure in the main text. The second row has had its excited state potential changed from $V = 0.7x^2$ to $V = 0.6x^2$, and the third row from $V = 0.3x^2$ to $V = 0.4x^2$. For the Morse oscillators (rows 4 and 5), the depth parameter for both the ground and excited electronic state has been doubled from $D = 10$ to $D = 20$, and the width parameter has been changed from $a = \sqrt{1/(2D)} = 0.2236$ to $a = \sqrt{1/(2D)} = 0.1581$. Also note that this changes the ω_{01} frequency which is used to define the period of oscillation for the Morse oscillators, T. The remaining parameters are identical to the main text case. The waiting time corresponds to a fraction of the period T.