

FIG. 3: (color online) Double-sided Feynman diagrams for all possible Liouville-space pathways contributing to the third-order optical response of a V-type system. The pathways for the  $S_I(\omega_\tau, T, \omega_t)$  and  $S_{II}(\omega_\tau, T, \omega_t)$  measurements are listed in top two rows; while the pathways for the  $S_{II}(\omega_\tau, T, \omega_t)$  measurement are listed in bottom two rows. The state numbers, 0, 1 and 2, correspond to  $4^2S_{1/2}$ ,  $4^2P_{1/2}$  and  $4^2P_{3/2}$  of potassium atoms.

ble Liouville-space pathways in the systems [33]. Two pathways contribute to each peak in the  $S_I(\omega_\tau, T, \omega_t)$  spectra; whereas for  $S_{II}(\omega_\tau, T, \omega_t)$  three pathways contribute to each diagonal peak (NA or NB) and only one pathway to each cross peak (NC or ND). Generally, the peak strengths are proportional to the sum over participating diagrams while the strength of individual diagram is proportional to  $\prod \mu_i$ , where index  $i$  runs from 1 to 4 and  $\mu_i$  is the transition dipole moment for each excitation step in each double-sided Feynman diagram. The ratio between the transition dipole moment for  $D_2$

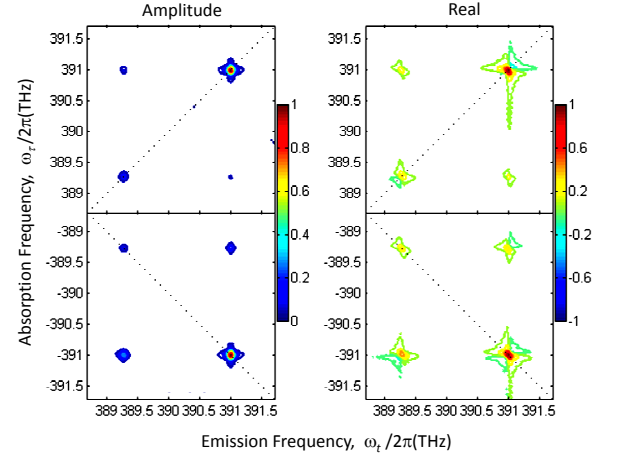


FIG. 4: (color) Calculated amplitude (left) and real-part (right) 2DFT spectra of potassium vapor for  $S_I(\omega_\tau, T, \omega_t)$  (bottom) and  $S_{II}(\omega_\tau, T, \omega_t)$  (top) measurements. The spectra are normalized to the most intense peaks.

transition,  $\mu_{D2}$ , to the dipole moment for  $D_1$  transition,  $\mu_{D1}$ , is approximately  $\sqrt{2} : 1$ . Assuming each quantum pathway has the same contribution to the peak strength, the peak strength ratio RA:RC:RD:RB is proportional to  $2\mu_{D1}^4 : 2\mu_{D1}^2\mu_{D2}^2 : 2\mu_{D2}^2\mu_{D1}^2 : 2\mu_{D2}^4$ , or relative values of 1:2:2:4. Similarly, the peak strength ratio in the  $S_{II}(\omega_\tau, T, \omega_t)$  measurement NA:NC:ND:NB is equal to 2:1:1:5, which agrees well with the experimental result.

The interaction between light and a closed two-level system can be described by the optical Bloch equations [34]:

$$\dot{\rho}_{00} = -\dot{\rho}_{11} \quad (1)$$

$$\dot{\rho}_{11} = -\gamma^{sp}\rho_{11} + \frac{i}{\hbar}\mu_{01}E(\rho_{01} - \rho_{10}) \quad (2)$$

$$\dot{\rho}_{01} = -\gamma^{ph}\rho_{01} + i\omega_{01}\rho_{01} + \frac{i}{\hbar}\mu_{01}E(\rho_{11} - \rho_{00}) \quad (3)$$

where  $\rho_{00}$  and  $\rho_{11}$  are density matrix elements for the ground and excited state population respectively, and  $\rho_{01}$  is the off-diagonal term of the density matrix.  $\gamma^{sp}$  and  $\gamma^{ph}$  are the population relaxation and dephasing rates respectively,  $\mu_{01}$  is the transition dipole moment,  $\omega_{01}$  is the resonant transition frequency and  $E$  is the electric field amplitude. We extended the equations to a multi-level system and numerically solved them [34, 35]. In the calculation,  $\gamma^{ph}$  is the total linewidth due to resonance and collision broadening. The induced polarization of the system is  $P = NTr(\mu\rho)$ . Then the electric field of the emitted signal is determined from the third order polarization [34]:

$$E(\tau, T, \omega_t) = \frac{2\pi L}{n(\omega_t)c} i\omega_t P^{(3)}(\tau, T, \omega_t) \quad (4)$$

where  $L$  is the sample thickness,  $n(\omega_t)$  is the index of refraction of the sample, and  $c$  is the speed of light in vacuum.  $S_I(\omega_\tau, T, \omega_t)$  and  $S_{II}(\omega_\tau, T, \omega_t)$  2DFT spectra