Quantum beats and Zeeman spectra of glyoxal from superposition of singlet and triplet states

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Decays of individual rovibronic levels of trans-glyoxal in its first excited singlet state are investigated in supersonic-jet conditions. Several rotational levels display oscillatory decay from coherent excitation of superposition of singlet and triplet states. Analysis yields a lower bound for the state-dependent coupling matrix elements $\nu_{ST} = 0.08–62$ MHz for the $S_1–T_1$ interaction. These matrix elements of the lowest singlet and triplet states show no simple systematic dependence on vibrational states, but the singlet state at greater $K$ quantum number couples to a few triplet states with $\nu_{ST}$ larger than for the state at lower $K$. The complex beat pattern is explored on varying the polarization of the laser beam relative to an external magnetic field. For state $N_{K_aK_c} = 3_{12}$ at excitation energy $25,254.36$ cm$^{-1}$, the Landé $g$ factor of its coupling triplet hyperfine levels is estimated. From comparison with the theoretical $g$ value for the Hund’s case (b), we found that for this state rotational angular momentum is conserved during singlet–triplet coupling. Irregular $M_F$ splittings and correlated beating frequencies resulting from resonance coupling between the singlet and triplet states are observed in the Fourier-transform spectra under the weak magnetic field condition. © 2002 American Institute of Physics. [DOI: 10.1063/1.1485770]

I. INTRODUCTION

Under the condition of no external field, when a zero-order state couples to a second state that possesses no oscillator strength, molecular quantum beats are exhibited from coherent excitation of these states. McDonald and co-workers$^{1–3}$ first applied quantum beats in fluorescence decay of polyatomic molecules. Huber and co-workers$^{4–14}$ extended this technique to combine a Zeeman field, and polarization detection with a high-resolution laser beam to study the hyperfine and Zeeman quantum-beat spectra, as well as molecular quantum beats, on free radicals and polyatomic and van der Waals molecules. Application of a magnetic field can split hyperfine components when the coupling state is nonsinglet; the split $2F + 1$ component beats can accordingly be separately resolved through Fourier-transform analysis to confirm assignments of quantum states and to measure Landé $g$ factors under the weak field condition.

Spectroscopy of the lowest excited singlet and triplet states of glyoxal have been studied for several decades.$^{15–38}$ Near the origin of state $\tilde{A}^1A_u^+$, interaction between states $S_1$ and $T_1$ of trans-glyoxal was investigated; extensive measurements were performed using level anticrossing,$^{21–27}$ and two-photon absorption combined with a Zeeman field by Kató et al.$^{34,35}$ In addition to accurate spectral parameters obtained for those electronic states, coupling of states $S_1$ and $T_1$ is proposed to involve vibronic spin–orbit interaction.

From this laboratory we presented results of analysis on rotationally resolved spectra of the transition $\tilde{A}^1A_u^+–\tilde{X}^1A_g^+$ for glyoxal in the wavelength range 395–404 nm under jet-cooled conditions.$^{39}$ This region is $\sim 2800–3300$ cm$^{-1}$ above the zero point of $\tilde{A}^1A_u^+$; all bands analyzed are attributed to trans-glyoxal. Fluorescence decays of ro-vibronic states with quantum beats were observed for the first time for glyoxal; their patterns arise from coherently exciting the mixed triplet and singlet states. Near the dissociation threshold on the triplet surface, the lifetime of the triplet state becomes shortened. This oscillatory behavior diminishes rapidly to display biexponential decay. Here we report results of detailed analysis of quantum-beat patterns of trans-glyoxal under a weak Zeeman field; we determined the lower bound for state-selected singlet–triplet coupling matrix elements and Landé $g$ factor and investigated conservation of quantum numbers of angular momentum for the singlet–triplet interaction.

II. EXPERIMENT

The experimental setup, described in detail elsewhere,$^{39}$ is merely summarized here. Transition of glyoxal in its system $\tilde{A}^1A_u^+–\tilde{X}^1A_g^+$ for the excitation wavelength range 390–417 nm was recorded in jet-cooled conditions at the resolution 0.04–0.15 cm$^{-1}$. Total emission was detected without dispersion by a photomultiplier mounted perpendicularly to both the molecular jet and the propagation direction of the laser beam. A digital oscilloscope (Tektronics, TDS-520D, bandwidth 500 MHz) served to record curves for fluorescence emission of nearly single ro-vibronic states of $\tilde{A}^1A_u^+$ with a stepsize 2 ns and 2000 data points in total; about 1000 laser shots were averaged for each decay trace. Fluorescence emission curves superimposed with quantum beats were recorded. Three Helmholtz coils around the detection chamber provided a weak external magnetic field; these coils also compensated the terrestrial magnetic field. The direction of magnetic field (B) was set to be parallel to the direction of...
the detector. With a rhomb polarizer the polarization of the laser beam was set to be either parallel or perpendicular to the magnetic field.

To improve resolution in the frequency domain, after subtraction of background scattering, we added zeroes to the signal traces to extend the data to 10 µs in calculating the Fourier transform. Deconvolution over the instrumental response function assumed to have a Gaussian shape with full width 7 ns at half maximum during Fourier transform served to correct the line intensity in the FT spectra. The correction applied in the region at greater frequencies is consequently greater than that at smaller frequencies.

III. RESULTS AND DISCUSSION

A. Quantum beats

In the wavelength region 393–418 nm, we detected states with oscillatory fluorescence decays, and searched systematically for quantum beats for individual ro-vibrational states from 393 to 404 nm. For excitation wavelengths smaller than 393 nm, decays with quantum beats were unobserved; instead curves display biexponential decay because the triplet state is coupled to a dissociation continuum. The linewidth of the triplet state increases and its interaction with the singlet state becomes efficient; this interaction approaches the intermediate case for intramolecular energy transfer. Experimental curves for fluorescence decay with modulated oscillation and their FT spectra under the earth magnetic field appear in Fig. 1. Detailed experimental results for all states measured with quantum beats are available in Ref. 40. Limited by the coherent width of the laser beam, only eigenstates separated within ~100 MHz are observed in the present work.

Trans-glyoxal is a nearly prolate rotor with an asymmetry parameter \( \kappa \approx -0.98 \). With two equivalent H atoms of nuclear spin \( I = 1/2 \), the total nuclear spin is either 1 or 0. In the present work, only vibrational states of \( \tilde{A}^1A_u \) with vibrational symmetry \( \tilde{5}^1\Gamma_L = a_x \) and \( b_x \) are analyzed; for \( a_x \) even \( K_c \) states have \( I = 0 \) and odd \( K_c \) states have \( I = 1 \), but for \( \tilde{5}^1\Gamma_L = b_x \) the total nuclear spin is reversed for even and odd \( K_c \) states (\( K_c \) is the rotational quantum number projected along the \( c \) axis). Trans-glyoxal follows a vector coupling case (\( b_{\beta} \)): \( ^{34}N + S = J, J + I = F \), in which \( N, S, \) and \( F \) denote rotational angular momentum, angular momentum of electron spin, and total angular momentum, respectively. For \( \tilde{a}^3A_u \) the hyperfine states are known to split mainly via
Fermi contact interaction; Katô et al. determined parameter $a_1 \rightarrow a_T$ to be 88 MHz\textsuperscript{34,35} and Lombard et al. obtained 82±3 MHz.\textsuperscript{23} Term values of individual rotational states at high vibrational energy of the triplet are estimated roughly with rotational and spin parameters deduced by Ramsay and co-workers\textsuperscript{31} for the ground vibrational state of the triplet electronic state. All fine structure splittings of rotational states of $\tilde{a}^3A_g$ greatly exceed 100 MHz but hyperfine splitting for the rotational state of small $N$ is 20–150 MHz, of magnitude, about the same order as the quantum-beat window. Figure 2 shows the fine and hyperfine structure of rotational state $N_{K_aK_c} = 2_{11}$ as an example. Hence, within the 100 MHz window, and according to known selection rules for the singlet–triplet interaction of glyoxal $\Delta I = 0$, $\Delta F = 0$, and $\Delta J = 0$,\textsuperscript{24} a singlet zero-order state is expected to interact with one hyperfine level for $I = 0$ and up to three for $I = 1$ for each vibrational level of the triplet. For $I = 1$, $F$ can be $S J - 1$, $S J$, and $S J + 1$, but the splitting of these hyperfine states for the singlet electronic state is small.

The quantum-beat signal generalized to the case of $N$ coherently excited eigenstates (one singlet coupled with $N - 1$ triplet states) shows, in total, $N(N - 1)/2$ beat frequencies. Hence, for a state with $I = 0$ the number of coupling vibrational levels of the triplet state can be determined from the number of beat frequencies. Because the asymmetry parameter $\kappa$ of glyoxal is near $-1$, transitions to $K$ doublets are unresolved experimentally when $K \geq 1$, but because $K$ doublet states belong to distinct nuclear spin states, under an applied magnetic field the split $M_F$ states enable us to deduce the $F$ quantum number, and consequently, to identify the $K$ doublet states.

Theories of fluorescence intensity superimposed with quantum beats are documented in the literature.\textsuperscript{3,41–43} Here we adopted notation and symbols used by Huber et al.\textsuperscript{4} To explain some FT spectra discussed below, we specifically show an expression for time-resolved fluorescence intensity $I(t)$ for the case $N = 3$:

$$I(t) = I_0 \left[ |C_{S_1}|^4 \exp(-\gamma_1 t/\hbar) + |C_{S_2}|^4 \exp(-\gamma_2 t/\hbar) + |C_{S_3}|^4 \exp(-\gamma_3 t/\hbar) + 2|C_{S_1}|^2 |C_{S_2}|^2 \exp(-\gamma_{12} t/\hbar) \cos \omega_{12} t \right. $$

$$+ 2|C_{S_1}|^2 |C_{S_3}|^2 \exp(-\gamma_{13} t/\hbar) \cos \omega_{13} t + 2|C_{S_2}|^2 |C_{S_3}|^2 \exp(-\gamma_{23} t/\hbar) \cos \omega_{23} t \]$$

\[.\]

The effective Hamiltonian is defined in terms of three eigenstates that constitute a linear combination of zero-order states singlet $|S\rangle$, and $|T_1\rangle$ and $|T_2\rangle$ of triplet with eigenvalues $E_i = \epsilon_i - (i/2)\gamma_i i = 1 - 3$. The symbols $C$ and $\gamma$ denote the coefficient of the zero-order state and the linewidth in an eigenstate, respectively. $\gamma_i = C_{S_i}^2 \gamma_5 + C_{T_1}^2 \gamma_{T_1} + C_{T_2}^2 \gamma_{T_2}$ and $\gamma_{ij} = (\gamma_i + \gamma_j)/2$. The eigenstate wave function is $|\psi_i\rangle = C_{S_i}|S\rangle + C_{T_1}|T_1\rangle + C_{T_2}|T_2\rangle$ and $|C_{S_1}|^2 + |C_{S_2}|^2 + |C_{S_3}|^2 = 1$.

The Fourier transform of $I(t)$ is

$$I(\omega) = \int_{-\infty}^{\infty} I(t) \exp(-i\omega t) dt$$

$$\equiv I_0 \left[ |C_{S_1}|^4 (\gamma_1/\hbar)/[\omega^2 + (\gamma_1/\hbar)^2] + |C_{S_2}|^4 (\gamma_2/\hbar)/[\omega^2 + (\gamma_2/\hbar)^2] + |C_{S_3}|^4 (\gamma_3/\hbar)/[\omega^2 + (\gamma_3/\hbar)^2] \right.$$

$$+ 2|C_{S_1}|^2 |C_{S_2}|^2 (\gamma_{12}/\hbar)/[\omega - \omega_{12} + (\gamma_{12}/\hbar)^2] + 2|C_{S_1}|^2 |C_{S_3}|^2 (\gamma_{13}/\hbar)/[\omega - \omega_{13} + (\gamma_{13}/\hbar)^2]$$

$$+ 2|C_{S_2}|^2 |C_{S_3}|^2 (\gamma_{23}/\hbar)/[\omega - \omega_{23} + (\gamma_{23}/\hbar)^2] + \text{imaginary part}. \]$$

FIG. 2. Energy diagram of fine and hyperfine sublevels for $N_{K_aK_c} = 2_{11}$ of triplet trans-glyoxal calculated with parameters from Ramsay et al. (Ref. 31) and Fermi contact parameter $a_1 = 88$ MHz (Refs. 34 and 35).
methylglyoxal,1 biacetyl,1 and propynal.5 The fact that “gateway” states with large $v_{ST}$ (greater than 100 MHz) reported elsewhere27,35 are not observed is limited by the quantum-beat window. The magnitude of $v_{ST}$ agrees generally with the weak-interaction mechanism—vibronic spin–orbit coupling. Although the value of $v_{ST}$ shows scatter, no dependence on vibrational level is evident here. Overall, for states within the range of energy investigated in the present work, states with $K_S=1$ have more beat frequencies than states of $K_S=0$, because state $K_S=1$ can couple to states $K_T=0, 1, 2$ of the triplet state whereas state $K_S=0$ only to $K_T=0$ and 1.

To obtain the dependence of $v_{ST}$ on rotation, we analyzed two vibrational levels $5^2\gamma^110^2\gamma^1$ and $5^2\gamma^18^2\gamma^1$ displaying most rotational states with quantum-beat patterns. Plots of $v_{ST}$ vs $J$ for $K_S=0–2$ appear in Fig. 4. For both vibrational states no dependence on rotational quantum number $J$ is obvious, but the zero-order state at greater $K$ quantum number couples to some triplet states with $v_{ST}$ larger than for states at smaller $K$. The matrix element for spin–orbit, singlet–triplet interaction derived by Stevens and Brand45 shows linear dependence on $K^2$ under $\Delta N=\Delta K=0$ and only slight dependence on $K$ for $\Delta N=\pm 1$ or $\Delta K=\pm 1$. Previous findings show that states $\tilde{A}^1A_y$ and $\tilde{A}^3A_y$ of glyoxal undergo vibronic spin–orbit coupling; $\tilde{A}^1A_y$ is thus coupled to $^3B_y$ and $\tilde{A}^3A_y$ is vibronically coupled to $^3B_y$.44,35 Because both $R_a$ and $R_b$ (rotation along the $a$ and $b$ axis, respectively) have symmetry $b_y$ in point group $C_{h}^2$, interacting states can have $\Delta K=0(R_a)$ or $\pm 1(R_b)$.45 Dupre et al.26 used the level crossing spectroscopy to determine the matrix elements as a function of rotational quantum numbers and compared it with the theoretical model of singlet–triplet coupling. Couplings following $\Delta K=0$ or $\pm 1$ are observed. They found no significant difference in vibrational states near the origin of $S_1$ for the magnitude of couplings. Our results for the high-energy region agree with their findings. From the strong dependence on $K$, current experimental data confirm that for these two vibrational levels, several triplet states are expected to interact with the singlet via $\Delta N=\Delta K=0$.

The lowest panel in Fig. 5 indicates three beat frequencies 23.0, 27.7, and 50.8 MHz for the state $3\gamma_1$ at excitation energy 25 254.36 cm$^{-1}$; the sum of frequencies of the former two lines is that of the third line (experimental accuracy for transformed lines is $\sim 0.1$ MHz). These three beat frequencies are hence related, and the number of coherently excited eigenstates is therefore three. All three lines have measurable intensity; the mixing coefficients $|C_{S2}|^2$ and $|C_{S3}|^2$ are thus not expected to be much smaller than $|C_{S1}|^2$. The weak-coupling approximation is inadequate for interaction of this state to the triplet. Coefficients $|C_{Sj}|^2$ can be estimated from ratios of areas among these three lines:

$$A(\omega_{ij})/A(0)=2|C_{Sj}|^2|C_{Sj}|^2/(|C_{S1}|^2+|C_{S2}|^2+|C_{S3}|^2)$$

with $|C_{S1}|^2+|C_{S2}|^2+|C_{S3}|^2=1$. Coefficients $|C_{S1}|^2$, $|C_{S2}|^2$, and $|C_{S3}|^2$ are accordingly calculated to be 0.508, 0.313, and 0.178, respectively. Experimental data indicate that a few states display similar behavior, for instance, state $1_{01}$ excited.

In the real part of the Fourier-transform equation, lines with Lorentzian shape exist at frequency $\omega=0$ and $\omega_{ij}=(\varepsilon_i-\varepsilon_j)/\hbar$. For $N=3$ we expect three beat frequencies $\omega_{12}$, $\omega_{13}$, and $\omega_{23}$. In a weak-coupling case, $|C_{S1}|^2\approx 1$, coefficient $|C_{S2}|\approx |C_{S3}|$ is nearly zero; the intensity of the third nonzero frequency peak would hence be negligible. From transformed spectra the peak areas are $A(0)$ and $A(\omega_{ij})$ at $\omega=0$ and $\omega_{ij}$, respectively, and

$$A_{\text{total}}=2A(0)+A(\omega_{12})+A(\omega_{13})+A(\omega_{23}).$$

For weak coupling, the coefficient $C_{Si}$ can be evaluated from ratios of these areas according to the following equations:

$$A_{\text{total}}=2(|C_{S1}|^4+|C_{S1}|^2|C_{S2}|^2+|C_{S1}|^2|C_{S3}|^2)$$

$$=2|C_{S1}|^2,$$  

$$A(\omega_{ij})/A_{\text{total}}=|C_{Sj}|^2.$$  

According to first-order perturbation theory, the coupling matrix element $v_{ST}$ is approximately

$$v_{ST}=|C_{Sj}|\omega_{ij}.$$  

Values of the state-resolved mixing coefficient $C_{Sj}$ and coupling matrix element $v_{ST}$ obtained from experiments under weak coupling, are available in Ref. 40. Because of the multimode character of our laser beam, the modulation can be averaged to some extent; the coupling matrix element reported is hence a lower bound of the true value. A plot of $v_{ST}$ obtained using Eqs. (4)–(6) vs excitation energy appears in Fig. 3 along with results of analysis of biexponential fluorescence decay curves obtained at greater excitation energy.39 The measured coupling matrix elements have a range 0.08–62 MHz (0.03–21 $\times 10^{-9}$ cm$^{-1}$), which has a magnitude of the same order as for acetaldehyde,44
Under the terrestrial magnetic field, $M_F$ states are readily split from having a significant proportion of triplet-state character. According to the number of splitting lines and the relative spectral intensity, the $F$ value is assigned to be unity. Most beat frequencies in the FT spectra show no related beat frequency, indicating that for most states an assumption of weak coupling is adequate.

B. Zeeman effect

To confirm quantum-state assignments and to measure Landé $g$ factors for states, we applied an external Zeeman field. Figure 5 shows split lines in FT spectra of state $3_{1/2}$ at excitation energy $25.254.36$ cm$^{-1}$ for magnetic field $B = 0 - 3.4$ G. Apodized spectra were obtained on biasing the long-lived fluorescence by multiplying the decay with a Gaussian function to resolve the lines; those are shown in Fig. 7 and in the upper trace of Fig. 8 for two polarization directions of laser beam relative to the magnetic field. Lines centered at $23.0$ and $27.7$ MHz split from the Zeeman field but the line at $50.8$ MHz becomes only broadened from $0.65$ ($B = 0$ G) to $0.85$ MHz ($B = 3.4$ G); the latter line after apodization splits to $50.8, 51.2$, and $51.8$ MHz. From the splitting spectra we evaluate $F$ to be $3$ for lines at $23.0$ and $27.7$ MHz. Because these three lines are related, they are all expected to have the same quantum number $F$. No state with another $F$ value is observed. We consequently assigned the zero-order rotational state resulting in oscillatory modulation to $3_{1/2}$ and $I = 0$ from known vibrational symmetry $a_g$ (determined from the rotational band structure; the vibrational quantum number for this state remains undetermined).

In Figs. 7 and 8 the split lines centered at $23.0$ and $27.7$ MHz show irregular spacing from $0.36 - 0.95$ and $0.60 - 0.95$ MHz, respectively with spacing increasing toward the high-frequency region. It is highly unlikely for a triplet state under such a weak field to have irregular $M_F$ splitting. For simplification, we consider a system with two levels $|T\rangle$ and $|S\rangle$; they are coupled with Hamiltonian $\hat{H}_{SO}$ and magnitude $\nu_{ST}$. The resulting two eigenstates $|k\rangle$ and $|k'\rangle$ with energy difference $\omega_{kk'} = \epsilon_k - \epsilon_{k'}$ are observed through the quantum-mechanical coupling of the two states. 

**FIG. 4.** Coupling matrix element $(\nu_{ST})$ from analysis of quantum-beat patterns plotted vs rotational quantum number $J$ for $K_a = 0 - 2$ states of vibrational level $5^2 \tilde{g} 7/2 8/1$ and $5^2 \tilde{g} 11/2 12/1$. 
beat frequency in the frequency domain and $\omega_{kk'} = (\Delta_{ST}^2 + 4\nu_{ST}^2)^{1/2}$, in which $\Delta_{ST}$ is the singlet–triplet detuning, i.e., the energy separation of the zero-order states. Eigenvalues of these two levels after diagonalization of the Hamiltonian with perturbation $\hat{H}_{SO}$ and $\hat{H}_Z$ (Zeeman term $= \mu_B B \cdot g_{S} \cdot S$) are formulated as

$$E_k(M_F, B) = \frac{E_S + E_T + \mu_B g_T M_F B}{2} \pm \left[ \frac{(E_S - E_T - \mu_B g_T M_F B)^2}{4} + \nu_{ST}^2 \right]^{1/2}. \quad (8)$$

The symbol $g_F$ represents the Landé $g$ factor of the zero-order triplet state and $\mu_B$ is the Bohr magneton. The opposite signs correspond to two eigenstates, $|k\rangle$ and $|k'\rangle$. Because the molecular Hamiltonian has rotational invariance, only states with $\Delta M_F = 0$ are coupled and $\nu_{ST}$ is assumed independent of $M_F$. When the term $\mu_B g_T M_F B$ is not much smaller than $\Delta_{ST} = E_S - E_T$, the spacing among $M_F$ states can be uneven. Using a first-order perturbation and Eq. (8), we have the best fits for the singlet–triplet detuning and coupling matrix element from the zero-field data to be 21.9 and 8.5 MHz, respectively, for the triplet state involving the state at 27.7 MHz separation. Then we varied the value of $g_F$ to obtain the best fit to the split data. The $g_F$ factor is hence 0.21 (0.16 for lines centered at 23.0 MHz). Deviations to the measured frequencies for a few lines are at most twice of our experimental resolution. This may indicate that the second order term of the singlet–triplet interaction needs to be included to obtain a better fit for the irregular spacings.

From equations below for $g_F$ and $g_T$ of triplet for Hund’s coupling case (b),

FIG. 5. Fourier-transform spectra of fluorescence decays of level 3_{1/2} via transition $^3P_0(2)$ at excitation energy 25 254.36 cm^{-1} and Zeeman field $B = 0$–3.4 G for $E_p\parallel B$ and $B = 3.4$ G for $E_p\perp B$ (the top trace). Wave numbers of lines are indicated in the lowest trace.

FIG. 6. Quantum-beat pattern in time-resolved emission decay trace (a) and the corresponding real part of Fourier-transform spectra (b)+(c) for state 1_{01} and excitation energy=25 125.8 cm^{-1}. In (c) the spectrum is apodized with a Gaussian function. The sum of beat frequencies labeled by the same letters $x$, $y$, and $z$ near 20 and 69 MHz equals the beat frequencies labeled with the corresponding letter near frequency 90 MHz.
we calculate $g_T$ to be 0.167, -0.5 and 0.667 for $N_T=J$, $(J+1)$ and $(J-1)$, respectively, given $J=F=3$ and $I=0$; for $I=0$, $g_F=g_T$. This experimental finding indicates that the coupled triplet has $N_T=J$. Because $J=N_S$, the rotational quantum number remains as a good quantum number. For the state $I_0$ shown in Fig. 6, because $g_T$ is large at low $J$, the splitting is readily observed at the Earth's magnetic field.

We simulated the transformed spectra for two directions of polarization according to a density-matrix formalism derived by Dubs et al.\textsuperscript{6} based on the theory of Fano and Macek;\textsuperscript{47} for detailed derivations please refer to those papers. Simulated spectra, with $E_k(M_F,B)$ calculated according to Eq. (8) and with the full width at half maximum fixed at 0.25 MHz for two geometries, are displayed in Fig. 8. The ratio of spectral intensity between lines centered at 23.0 and 27.7 MHz is obtained numerically from the best fit to the spectrum recorded at detection geometry $E_p\parallel B$. The same ratio is applied in simulating the spectrum at geometry $E_p\perp B$. Deviations from the experimental curve for spectral intensity might arise from the multimode character of the laser beam and for other unknown reasons, but overall features of simulated spectra reproduce main features of experimental spectra.

On scrutiny of these split frequencies, we found that a sum of split frequencies centered at 23.0 and 27.7 MHz equals the split frequencies at 51 MHz ($\sim$ related lines are labeled with the same letters in Fig. 7). A similar behavior holds for lines in Fig. 6. Lines at 51 MHz, from separation between uneven spaced lines are 23.0 and 27.7 MHz. Hence, even at $B=3.4$ G the overall splitting at 51 MHz is not much broadened as those in the other two lines. Because only separations among these eigenstates are obtained from the beat frequencies, not their absolute positions, one possible relative position of these three eigenstates is displayed in Fig. 9. An alternative possibility for these eigenstates has reversed all positions plotted in Fig. 9 as well as the sign of $M_F$, so
that under a magnetic field positive $M_F$ states lie at greater energy. For state $3_{12}$ shown here, three states are involved that ought to be considered simultaneously, but such a procedure makes the deduction of values of those parameters difficult. The values estimated based on a two-level system and first-order perturbation theory are expected to deviate from true values, but simulated spectra based on the model agree qualitatively with experimental data and this simple model can serve to explain the experimental findings.

IV. CONCLUSION

From analysis of quantum-beat data, we used the information of beat amplitudes and frequencies to obtain a lower bound of state-resolved coupling matrix elements for rovibrational states of $\tilde{A}^1A_u$ of glyoxal. On applying an external magnetic field we measured the Landé $g$ factor for one triplet state coupling to $3_{12}$ at $25254.36$ cm$^{-1}$ to be $g_T = 0.21$ and all coupling triplet states are assigned to $F = 3$. Only for $N_T = J$ the calculated $g$ value for Hund’s case (b) agrees with the experimental value; thus this state crosses to the triplet surface expected to be at $\Delta N = 0$. The $M_F$ separations are irregular in frequency-resolved FT spectra. In this case this singlet state is at resonance with two triplet states; the coupling is comparable to the Zeeman splitting to yield variable $M_F$ separations. Another state $1_{01}$ is observed to display similar strong coupling behavior. However, most beat frequencies in the Fourier-transform spectra show no related beat frequency, implying that the weak coupling between the singlet and triplet states is adequate.

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40. “See the EPAPS Document No. EJCPAS6-117-011228 for table containing lists of states with quantum beats and the coupling matrix elements, mixing coefficients and linewidths in the Fourier-transform spectra. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.”