Perturbation facilitated two-color four-wave-mixing spectroscopy of C_3

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Perturbation-facilitated two-color resonant four-wave-mixing spectroscopy is realized to access the (dark) triplet manifold of the C_3 molecule from the singlet $\tilde{X}^1\Sigma_g^+$ ground state. The inherent non-linear signal dependence and coherence of the technique result in a favorable detection of the excited triplet states of interest. The observation of a newly found $^3\Delta_u$ electronic state is achieved by a two-step excitation *via* “gate-way” levels (i.e., singlet-triplet mixed levels). Additionally, by fixing the probe laser on a transition exhibiting mainly triplet-triplet character and scanning the pump laser, we demonstrate an effective spin-filtering in a four-wave mixing measurement where only transitions to the perturber $^3\Sigma_u^-$ state appear exclusively in an otherwise congested spectral range of the Comet band. *Ab initio* calculations of excited triplet states complement our analysis with the electronic assignment of the observed resonances. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4825198>]

I. INTRODUCTION

The concept of multi-photon transitions in an atom or a molecule has been predicted by Göppert-Mayer in 1931.¹ Few decades later multi-photon molecular spectroscopy was widely accepted as a powerful method to observe molecular excited states.^{2,3} Perturbative approach multi-photon processes are treated by one or several successive transitions essentially governed by the molecular electric dipole operator $\hat{\mu}_\alpha$ with, respectively, $\alpha = x, y, z$. Selection rules are determined by the symmetries of the states coupled and by the symmetry of the dipole moment operator, i.e., $\Gamma_2 \otimes \Gamma_{\hat{\mu}_\alpha} \otimes \Gamma_1$. In dipole approximation two states of different spin-multiplicities cannot be coupled by the electric dipole operator except for states with spin-orbit interaction. Levels that are inaccessible by optical transitions are called dark states in contrast to the dipole allowed transitions to bright states. It is important to mention that the spectroscopically dark states can be dynamically active and play an important role in energy flow processes governing intra- and inter-molecular energy redistribution.

Perturbation effects provide ways to observe dark states on optically accessible bright states by applying double resonance techniques.^{4–6} In fact, perturbation facilitated optical-double resonance (PFOODR) spectroscopy has been used to access dark triplet spin states from singlet ground states *via* singlet-triplet mixed levels as intermediate window states in two-step excitations. Mainly alkali metal dimers were studied by perturbation facilitated spectroscopy (see Refs. 7–9 and references therein). The studies have been performed by applying methods such as fluorescence excitation,¹⁰ dispersed fluorescence (DF) detection,^{9,11} or continuous-wave optical triple resonance spectroscopy.¹² Recently, a perturbation-assisted approach to prepare population at high vibrational states of CO ($X^1\Sigma^+$) was demonstrated.¹³

In this work we apply, for the first time to the best of our knowledge, two-color resonant four-wave mixing (TC-RFWM) to perform PFOODR spectroscopy. We extend the earlier work on diatomic molecules by taking advantage of the coherent background-free TC-RFWM technique offering an excellent sensitivity and selectivity which is adequate to investigate the triplet manifold of the polyatomic C_3 molecule exhibiting a $\tilde{X}^1\Sigma_g^+$ ground state. The high dynamic range and the favorable state selectivity of the method resulted in deperturbation studies unraveling the spin-orbit interaction of a dark state with a bright state in C_2 ^{14,15} as well as Rydberg-valence state interactions in NO.¹⁶

The tri-carbon emission at 405 nm has been observed for the first time in the tail of a comet by Huggins in 1882.¹⁷ C_3 was identified in diffuse interstellar clouds through absorption in the same spectral range.^{18,19} In 1951 Douglas observed the 405 nm band at a high resolution in the laboratory.²⁰ A spectroscopic analysis of the so-called Comet band $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ has been performed by Gausset *et al.*²¹ In addition to the significance of C_3 in space, the radical is suggested as a potential precursor for soot formation in flames.²² The $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ spectral signature appears upon irradiation of soot particles in a flame.²³ Several crossed molecular beam experiments supported by *ab initio* calculations have analyzed possible pathways towards the formation of polyaromatic hydrocarbons (PAHs) under high-temperature flame conditions.^{24–26}

The spectroscopy and dynamics of the linear- $C_3(X^1\Sigma_g^+)$ ground state were subjects of intense studies.^{22,27–31} A rovibrational analysis confirmed the linear ground-state structure with a low bending vibrational frequency of 63 cm^{-1} .²¹ The ground-state potential energy surface (PES) has been found to be anharmonic with a large amplitude bending motion.^{27,32} A number of quantum chemical calculations have been performed to examine cyclic C_3 structures.^{33–35} The

low-frequency bending motion is a feasible deformation path to generate the equilateral triangle. According to studies of Fueno and Taniguchi,³⁴ the lowest $^3\Pi$ states undergo isomerization into a cyclic structure *via* an asymmetric transition state. These cyclic and bent C_3 structures were not observed experimentally. Though they may play an important role in the reaction pathways to the formation of PAHs, and render the C_3 triplet states as an attractive object for further studies. Contrary to the singlet manifold, data available for triplet states are limited.^{36,37} As will be demonstrated in the following, the perturbation-facilitated two-color four-wave-mixing (PF-TC-FWM) technique is able to provide important benchmarks for the *ab initio* calculations of the equilibrium geometries and origins of the excited triplet states.

II. EXPERIMENT

The experiments are performed in a molecular beam apparatus designed for simultaneous linear and non-linear spectroscopic measurements of stable and transient molecules.³⁸ C_3 in the ground $\tilde{X}^1\Sigma_g^+$ state was prepared in the molecular beam environment by expansion of $\approx 1\%$ acetylene diluted in Ar buffer gas through a solenoid valve (General Valve, Parker).³⁹ Typical backing pressures are between 5 and 11 bars. The molecular pulse has a duration of about 750 μs . Prior to the expansion, the pulse passes through a multichannel flow-body producing a flow which is pertinent to the slit geometry of the discharge source.⁴⁰ The slit-expansion geometry increases the interaction volume between the crossing area of four-wave mixing laser beams and the molecular jet (see Fig. 1). Compared to a more common pinhole expansion, the sensitivity of the method can be enhanced by nearly two orders of magnitude due to the quadratic dependence of the four-wave mixing signal on interaction length.⁴¹ A pulsed voltage of -800 to -900 V and ≈ 2 μs duration is applied to the electrodes prior to the expansion zone. Trigger time delays between the discharge and the molecular beam pulse were optimized to the maximum production of C_3 molecules which were probed by four-wave mixing and/or laser

induced fluorescence ≈ 5 mm downstream of the expansion region.

The optical setup for TC-RFWM is established by applying two separately pumped dye lasers (narrowscan, Radiant Dyes). The specified bandwidth of both laser systems is ≈ 0.04 cm^{-1} . To obtain optimized spatial intensity profiles, both beams pass through spatial filters. Absolute wavelength calibration is performed for each scan step by a wavemeter (High Finesse/Ångström, WS6). A forward BOXCARS configuration is set up by a combination of optical components as detailed in Ref. 42 and outlined briefly in the following. A 1000 mm focal length achromatic objective (L1) focuses three parallel propagating laser beams to pass along the three main diagonals of a parallelepiped and cross with a small angle of 1° (see Fig. 1). These beams are arranged orthogonally to the propagation direction of the molecular beam, hence, eliminating the Doppler broadening. The wave vectors, $\vec{k}_i$, of the interacting beams fulfill the phase-matching condition

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4, \quad (1)$$

and generate the signal beam $\vec{k}_4$ along the forth (dark) diagonal. The two laser beams of equal frequencies are usually referred to as PUMP beams $\vec{k}_1, \vec{k}_2$, and the third beam, $\vec{k}_3$, as PROBE beam. The signal beam is collimated by the achromatic objective (L2) (FL = 1000 mm). A set of spatial (SSF) and spectral (SF) filters remove scattered light and unwanted fluorescence along the ≈ 2 m propagation of the signal in free-space. Further reduction of the stray light is achieved by a 30 mm focal lens and a 50 μm pinhole in front of a photomultiplier tube. Typically 20-30 pulses are averaged per scan step (5×10^{-4} nm/step) of the dye-laser on the oscilloscope and transferred to the personal computer (PC) for further analysis.

III. RESULTS AND DISCUSSION

The intermediate levels $|i; Jp\rangle$ addressed in this work are related to the rotational $J = 5$ level of parity p of the (000) $\tilde{A}^1\Pi_u$ state which is perturbed by a nearby lying triplet state of $^3\Sigma_u^-$ symmetry by spin-orbit coupling. The perturbation gives rise to mixed states exhibiting both singlet and triplet character.⁶ Such mixed states may be expressed as a superposition of unperturbed, zero order rovibronic states $|j^{(0)}; Jp\rangle$ with respective mixing coefficients c_{ji} :

$$|i; Jp\rangle = \sum_j^n c_{ji} |j^{(0)}; Jp\rangle, \quad (2)$$

where n is the number of effectively interacting states. Here, zero order states are product states characterizing an (adiabatic) electronic state of well defined spin multiplicity and a well defined vibrational state. As the total angular momentum and parity are conserved, they are equal on the right and left-hand sides of Eq. (2).

In order to identify better the intermediate levels in question here, we follow Ref. 6, but simplify the picture by including only one perturber state ($^3\Sigma_u^-$). We might then expect to

FIG. 1. Experimental arrangement: *M* – Mask used for laser beam alignment. *L1*, *L2* – 1000 mm focal length focusing and collimating lenses, respectively. *RS* – Radical source for C_3 . *MB* – Molecular beam. *SSF* – Set of spatial filters. *SF* – Spectral filter. *PMT* – Photomultiplier tube with the integrated amplifier.

FIG. 2. Energy level diagram showing the applied UNFOLDED (a) and SEP (b) double-resonance schemes by TC-RFWM. Gateway mediated intersystem-crossing from the $\tilde{X}^1\Sigma_g^+$ singlet ground state $|g\rangle$ to a triplet final state $|f\rangle$ is achieved by the UNFOLDED scheme and selecting the mixed singlet-triplet rovibronic intermediate level $|i\rangle$ with $\approx 80\%$ triplet character ($|\psi_2\rangle$). The spacing of the perturbed level pair is shown exaggerated in the figure.

have two intermediate levels:

$$|\psi_1\rangle = c_{11}|\tilde{A}^1\Pi_u\rangle + c_{21}|^3\Sigma_u^-\rangle, \quad (3)$$

$$|\psi_2\rangle = c_{22}|^3\Sigma_u^-\rangle + c_{12}|\tilde{A}^1\Pi_u\rangle, \quad (4)$$

with $c_{11} = c_{22}$ and $c_{12} = -c_{21} = \sqrt{1 - c_{11}^2}$, where we take into account the molecular constants for the perturbing $^3\Sigma_u^-$ from the deperturbation analysis of Zhang *et al.*,⁶ to deduce a mixing coefficient of $|c_{12}|^2 \approx 0.2$ for the two $J = 5$ levels. For brevity, the quantum numbers for the vibrational and rotational levels, as well as the parity quantum numbers, are omitted in Eqs. (3) and (4). The corresponding interaction between the $|^3\Sigma_u^- \rangle$ and $|\tilde{A}^1\Pi_u\rangle$ states scales with a square of the overlap integral between vibrational wave-functions (Franck-Condon factor).

The presence of the perturbation at $J = 5$ represents the “gate-way” to the triplet manifold for the TC-RFWM experiments. To characterize the involved transitions, two double-resonance schemes have been applied that are shown in Fig. 2. For the UNFOLDED (Ξ -scheme), the two PUMP beams of equal frequency link the ground state $|g\rangle$ and a level $|i\rangle \in \{|\psi_1\rangle, |\psi_2\rangle\}$ of the perturbed intermediate pair. Subsequently, the PROBE beam resonant with the $|f\rangle - |i\rangle$ transition excites the higher lying final state $|f\rangle$ and generates a SIGNAL beam of the same frequency. Alternatively, the energy level scheme for the stimulated-emission pumping (SEP) type experiment (Λ -scheme) is depicted on the right-hand side. For both Ξ - and Λ -schemes, the final $|f\rangle$ -state is connected to the ground $|g\rangle$ -state by optically allowed transitions, thus facilitating the direct assignment of the observed state by stringent two-color selection rules.

A. TC-RFWM measurements via perturbed intermediate ψ_1 and ψ_2 states

Results from TC-RFWM experiments are given in Figs. 3 and 4. The inverted spectrum in Fig. 3 is obtained by tuning the PUMP lasers of equal frequency to the perturbed P(6) transition of the Comet band ($000-000$) $\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma_g^+$ at $24\,669.697\text{ cm}^{-1}$ and scanning the PROBE. The excited $|\psi_1\rangle$ intermediate level exhibits $\approx 80\%$ singlet character. Subsequently, the PROBE laser is scanned in the spec-

FIG. 3. SEP transitions by applying TC-RFWM from the ground state (000) $\tilde{X}^1\Sigma_g^+$ via $|\psi_1\rangle$ and $|\psi_2\rangle$ exhibiting $\approx 20\%$ and 80% triplet character, respectively. P(6) and R(4) are SEP transitions to the vibrationally excited (022) level of the ground state $\tilde{X}^1\Sigma_g^+$. The lower trace is shifted by 1.72 cm^{-1} unambiguously indicating SEP type transitions. See text for details.

tral region near $20\,560\text{ cm}^{-1}$. Two relatively intense SEP type transitions, i.e., P(6) and R(4) are observed. These lines connect the upper $J = 5$ level of the (000) $\tilde{A}^1\Pi_u$ level and the $J = 4$ and $J = 6$ levels of the vibrationally excited (022) $\tilde{X}^1\Sigma_g^+$ ground state. Alternatively, excitation of the perturbing $^3\Sigma_u^-$ state ($|\psi_2\rangle$), which is separated by 1.72 cm^{-1} only, yields a weak signal at P(6) and R(4) transitions (upper trace in Fig. 3). Extra resonances denoted by an asterisk arise because of a spectral overlap of the PUMP laser with the Q-branch of the bright $|\psi_1\rangle$ state.

On the other hand, the upper trace in Fig. 4 is obtained by tuning the PUMP lasers to the perturbing P(6) $^3\Sigma_u^- - \tilde{X}^1\Sigma_g^+$ transition connecting the ground state with the $|\psi_2\rangle$ level

FIG. 4. UNFOLDED transitions by applying TC-RFWM from the ground state (000) $\tilde{X}^1\Sigma_g^+$ via $|\psi_1\rangle$ and $|\psi_2\rangle$ exhibiting $\approx 20\%$ and 80% triplet character, respectively. The lower trace is shifted by -1.72 cm^{-1} unambiguously indicating UNFOLDED transitions. The inset shows three relevant Feynman diagrams, assuming that only the C_3 ground state is populated $|g\rangle \rho_{gg}^{(0)} \langle g|$, where $\rho_{gg}^{(0)}$ is the density matrix element for the magnetic sublevel m_g at thermal equilibrium.

exhibiting $\approx 80\%$ triplet character. Three major transitions with substantial intensities (please note the scaling factor of 10^{-2} in the ordinate) are observed around $21\,145\text{ cm}^{-1}$. By contrast, the excitation *via* the $|\psi_1\rangle$, just 1.72 cm^{-1} below $|\psi_2\rangle$, shows that the peaks are present exhibiting, however, an intensity close to the noise level. The frequency axis for the latter is shifted by -1.72 cm^{-1} indicating unambiguously an UNFOLDED transition to a high lying state. Note, that shifting the PROBE frequency axis by the $-\Delta$ or $+\Delta$, where Δ is the energy difference between the two intermediate states, provides the information on the observed double-resonance scheme, i.e., UNFOLDED or SEP, respectively.

The spectrum in Fig. 4 shows a three-line pattern measured from the $J = 5$ intermediate state. The singlet-triplet mixing is sufficiently strong to perform UNFOLDED double-resonance experiments involving intermediate states of the $^3\Sigma_u^- (= |\psi_2\rangle)$ for $4 \leq J \leq 16$. From these spectra, a characteristic Q-branch is recognizable by the minor energy difference relative to the neighbouring J -lines. The appearance of the Q-branch is a clear indication that $|f\rangle$ is a Π_g -state. Note that Saha and Western³¹ performed double-resonance experiments for the Renner–Teller analysis of the excited $^1\Delta_g$ state and observed a similar rotational pattern for a vibronic $\Pi_g - \Sigma_u^+$ transition in the singlet manifold.

Considering the triplet character of the intermediate levels $|\psi_1\rangle$ and $|\psi_2\rangle$ of $\approx 20\%$ and 80% , respectively, and assuming a P(5), Q(5), and R(5) rotational structure, the final state $|f\rangle$ is likely a triplet state of $^3\Pi_g$ vibronic symmetry. Further evidence of the triplet character of the $|f\rangle$ state is presented and discussed in Sec. III D below.

B. The dependence of RFWM signal intensity on the intermediate state mixing coefficient c_J

A diagrammatic perturbation theory and spherical tensor formalism were used to derive FWM signal expressions.^{43,44} The induced polarization of a medium is defined as $P_{\text{RFWM}}^{(3)} = N\text{Tr}(\hat{\mu}\rho^{(3)})$ a product of total number of absorbing molecules N , a trace operation $\text{Tr}(\dots)$ over the scalar dipole moment operator $\hat{\mu}$, and a third-order density matrix term $\rho^{(3)}$. For a full description of $\rho^{(3)}$ it is important to account for the different time ordering of photon-matter interactions.⁴⁵ The inset of Fig. 4 shows a set of double-sided Feynman diagrams contributing to the third order nonlinear susceptibility $\chi_{ijkl}^{(3)}$.^{45,46}

The resonant FWM signal intensity is proportional to the modulus squared of the third-order nonlinear polarization Eq. (5):

$$I_{\text{RFWM}} \propto \frac{1}{2} |P_{\text{RFWM}}^{(3)}|^2 = \frac{1}{2} \left| \epsilon_0 \frac{3}{2} \chi_{\text{RFWM}}^{(3)}(-\omega_4, \omega_1, \omega_3, -\omega_2) E_1 E_2^* E_3 \right|^2. \quad (5)$$

The spherical tensor solution of the four-photon matrix element product in $\chi_{\text{RFWM}}^{(3)}$ (for a detailed discussion, see Ref. 44 and references therein) factorizes the FWM signal expression into Einstein coefficients B_1 and B_3 , geometrical

factors $G_F^T(\epsilon_4, \epsilon_1, \epsilon_3, \epsilon_2; J_g, J_i, J_f)$ where $\epsilon_1, \epsilon_2, \epsilon_3$, and ϵ_4 are polarization unit vectors for fields $j = 1, 2, 3, 4$, line-shape functions $L(\omega_1, \omega_3)$, laser intensities I_1, I_2, I_3 , and the initial ground-state population N_g . Equation (6) allows an independent evaluation of geometrical factors and Einstein coefficients. The geometrical factors are polarization dependent and yield spatial information for magnetic sublevels m_J of the molecular ensemble in the laboratory frame.⁴⁷ B_1 and B_3 represent the interaction of target species with the resonant laser fields in the molecular frame:

$$I_{\text{RFWM}} \propto N_g^2 B_1^2 B_3^2 I_1 I_2 I_3 \times L(\omega_1, \omega_3)^2 G_F^T(\epsilon_4, \epsilon_1, \epsilon_3, \epsilon_2; J_g, J_i, J_f)^2. \quad (6)$$

Einstein coefficients are written *via* a square of the reduced matrix element $\langle \mu^{(1)} | \rangle$ for the involved transitions $|g\rangle, |i\rangle \in \{|\psi_1\rangle, |\psi_2\rangle\}, |f\rangle$:

$$B_1 = B_{g,i} = \frac{2\pi^2}{3\epsilon_0 h^2} \frac{|\langle i | \mu^{(1)} | g \rangle|^2}{2J_g + 1}, \quad (7)$$

$$B_3 = B_{i,f} = \frac{2\pi^2}{3\epsilon_0 h^2} \frac{|\langle f | \mu^{(1)} | i \rangle|^2}{2J_i + 1}. \quad (8)$$

The relevant diagrams contributing to $\chi_{\text{RFWM}}^{(3)}$ are shown in the inset of Fig. 4. The first two diagrams (from the left to the right) describe the PROBE beam scattering on the PUMP-induced population grating in the intermediate state $|\psi_{1,2}\rangle$. The third diagram may be interpreted as a coherence between $|g\rangle$ and $|f\rangle$ induced by a sequential absorption of a PUMP and a PROBE photon. In this case, the RFWM signal is emitted when the second PUMP photon is absorbed to the intermediate $|\psi_{1,2}\rangle$ state. For all three diagrams, the signal emerges in the “phase-matched” direction, Eq. (1), and has the frequency $\omega_4 = \omega_1 + \omega_3 - \omega_2$ ($\omega_1 = \omega_2 \neq \omega_3$).

The optimal conditions to observe $|f\rangle$ levels of triplet spin-symmetry through the gateway $|\psi_1\rangle$ or $|\psi_2\rangle$ states are determined by inserting Eqs. (7) and (8) and Eqs. (3) and (4) into Eq. (6), this gives the eighth power of the mixing coefficients in the signal intensity. Considering the PUMP resonantly tuned to a $|\psi_2\rangle$ state with $\approx 80\%$ triplet character and a PROBE resonant to a triplet $|f\rangle$ final state, the FWM signal is scaled by a factor of $(|c_{12}|^8 = 0.2^4) \times (|c_{22}|^8 = 0.8^4)$, respectively. Similar reasoning holds for intermediate excitation *via* ψ_1 and transitions within the singlet manifold.

It is important that the RFWM signal depends on the eighth power of the mixing coefficient. Linear methods such as absorption spectroscopy have a quadratic dependence on the mixing coefficient. Stimulated emission pumping and other double-resonance methods based on sequential absorption of two photons have quadratic dependence on c_J for each consecutive step. The four-wave mixing eighth-power functional relationship between c_J and the observable signal facilitates a spin-symmetry assignment of a final state (e.g., by the observation of line-strength propensities for corresponding intermediate states). The eighth-power law appears to be of an exceptional advantage for the selectivity of the method which makes it rather insensitive to small perturbations. Although, in order to measure J -dependent spectra containing spin-forbidden transitions the potential energy surfaces

FIG. 5. PFOODR spectrum by tuning the PROBE laser to several overlapping Q lines in the ${}^3\Pi_g$ - ${}^3\Sigma_u^-$ ($=|\psi_2\rangle$) vibronic system and scanning the PUMP lasers. Exclusively transitions from the ground state $\tilde{X}^1\Sigma_g^+$ to the perturbing ${}^3\Sigma_u^-$ state are observed showing further evidence that the final state exhibits substantial triplet character. For comparison, a simulation of the Comet band absorption spectrum is shown at the bottom where the significant features are governed by the $\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma_g^+$ transition. The inset (a) shows the level scheme and the coherence diagram contributing to a RFWM signal. The inset (b) shows potential energy surfaces of interacting ${}^3\Sigma_u^-$ and $\tilde{A}^1\Pi_u$ electronic states vs. J . Symmetry (even/odd) – $\oplus$: e(+/-) and $\ominus$: f(-/+). Note that the unknown electronic $P=1$ state perturbs $\tilde{A}^1\Pi_u$ only in the $1 \leq J \leq 3$ range.⁶

of two intermediate states should strongly interact in a wide range of rotational levels (e.g., in the present work spin-orbit interaction is sufficiently strong in the $4 \leq J \leq 16$ range, see Fig. 5(b)). The challenge of weak spin-orbit interaction might be circumvented by the selective Stark/Zeeman tuning of the magnetic sublevel m_J of a dark state to interact with the m_J of a bright state.

C. Saturation behavior of the intermediate states ψ_1 and ψ_2

For the applied pulse energies one should be cautious of the signal saturation behavior which consequently affects the intensity ratio between chosen $|\psi_1\rangle$ and $|\psi_2\rangle$ intermediate states. Considering a strong PUMP beam coupling the ground state with a dark $|\psi_2\rangle$ or a bright $|\psi_1\rangle$ state with the transition dipole moments evaluated in Table I, the contribution of the PUMP beam to the four-wave mixing signal intensity is balanced by saturation for both ψ_j - $\tilde{X}^1\Sigma_g^+$ transitions ($j = 1, 2$). The estimated spectral irradiance which saturates the PUMP transition is at least three orders of magnitude inferior to the spectral irradiance applied in current experiments. This significant saturation level is also reflected in the observed power-broadened linewidth of ≈ 12 GHz. A weak PROBE explores the intermediate state population grating giving rise to a $|c_{22}|^8$ and a $|c_{21}|^8$ signal intensity depen-

dence of the ${}^3\Pi_g$ - ψ_2 and ${}^3\Pi_g$ - ψ_1 transitions, respectively. The RFWM signal intensity ratios for the observed P, Q, and R branch resonances to the ${}^3\Pi_g$ state (Fig. 4) are on the order of 250 for two intermediate states $|\psi_1\rangle$ and $|\psi_2\rangle$. This value is in a qualitative agreement with the ratio of the singlet-triplet mixing coefficients $|c_{22}|^8/|c_{21}|^8 = 2^8 = 256$.

TABLE I. Oscillator strength, transition dipole moment, and saturation intensities.

Line	Life-time ^a ns	Oscillator strength f_{gi} ^b	Dipole moment $\times 10^{-29}$ (C m)	Saturation intensity (W/m ²) ^c
$P(4) \tilde{A}^1\Pi_u$	202	0.0243	0.3416	62.01
$P(4) {}^3\Sigma_u^-$	786	0.0063	0.1732	15.93
$R(2) \tilde{A}^1\Pi_u$	223	0.0221	0.3251	56.17
$R(2) {}^3\Sigma_u^-$	2190	0.0022	0.1037	5.72

^aBased on the life-time measurements of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ band with an inclusion of the perturber ${}^3\Sigma_u^-$ state, Ref. 6.

^bElectronic oscillator strength $f_e = 0.033$ measured in Ref. 48 at 3200 K.

^cIf saturation intensity is calculated for the Rabi frequency $\Omega_{sat} = \sqrt{\Delta\nu_L \Gamma_0}$, when a laser bandwidth is large compared to a coherence life-time $\Delta\nu_L \gg \Gamma_{ig}$. Saturation intensity for the PUMP transition is ≈ 7.5 kW/m². This value is about three orders of magnitude lower than experimentally applied PUMP intensities. See text and Ref. 49 for details.

D. “The spin filter” TC-RFWM measurement

Further evidence for the triplet character of the final state $|f\rangle$, which is observed by applying UNFOLDED PF-RFWM via the $|\psi_2\rangle$ intermediate state, is shown in Fig. 5. Here, PF-RFWM spectroscopy is performed by tuning the PROBE laser to the narrowly spaced Q-branch region and scanning the PUMP lasers in the spectral region of the Comet band ($000 - 000$) $\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma_g^+$. The RFWM coherence is described by the double-sided diagram shown in Fig. 5(a). In the spectrum, exclusively P and R transitions are observed with significant intensities that involve the intermediate perturbing state $^3\Sigma_u^-$ with $J = 4-16$. For comparison, a typical absorption spectrum of the Comet band is simulated and shown inverted in the lower trace. The observation is rationalized in a straightforward manner by assuming an intermediate level labeling of several overlapping Q-lines in the $^3\Pi_g-^3\Sigma_u^- (|f\rangle - |\psi_2\rangle)$ system which are addressed simultaneously by the PROBE laser. It is important to mention that the perturber transitions are generally weak and difficult to observe in common absorption spectroscopy. In fact, a detailed analysis has been achieved only recently by applying cavity ring-down and time-resolved LIF measurements.^{6,50}

It should be noted that the intensity distribution of observed rotational lines does not reflect the population distribution among rotational levels of the C_3 ground state. There are two reasons for a non-thermal J -dependence of the measured intensities in the spectrum of Fig. 5. On the one hand, the rovibronic spectrum is truncated by the eighth power of the mixing coefficient c_J (*vide supra*) which in turn depends on the interaction of $\tilde{A}^1\Pi_u$ and $^3\Sigma_u^-$ (Fig. 5(b)). On the other hand, the partial spectral overlap of the PROBE laser with the narrowly spaced Q-branch limits the number of J levels that are observed.

E. *Ab initio* calculations of the C_3 triplet manifold

To shed more light on the C_3 triplet manifold, *ab initio* calculations have been performed at the multi-reference configuration interaction (MRCI) level with the MOLPRO package.⁵¹ Active orbital spaces and reference states were obtained by applying complete active space self-consistent field (CASSCF) theory.⁵² The MRCI calculations were conducted with equal bond lengths of $r = 1.2950$ Å.³¹ The internally contracted MRCI method of Werner and Knowles⁵³⁻⁵⁶ was used in a complete active space (CAS) of 12 electrons in 12 orbitals. This CAS is the complete valence active space. The results of the cluster Davidson corrected transition energies ΔE obtained with the aug-cc-pVTZ basis set are summarized in Table II. We estimate the accuracy of the calculated values to be better than 200 hc cm^{-1} (where h is the Planck constant and c is the speed of light in vacuum), both with respect to the basis size used as well as with regard to the inclusion of additional electronic correlation.

The newly measured excited state of $^3\Pi_g$ vibronic symmetry (i.e., $\Gamma_{vib} \otimes \Gamma_{el}$) can be assigned to a few possible final electronic states: Δ_u , $^3\Sigma_u^-$, or $^3\Pi_g$ appearing in the vicinity of $45\,000$ cm^{-1} (Table II). Selection rules prohibit transitions between $u \leftrightarrow u$ (ungerade) states. As a consequence,

TABLE II. Electronic term values of C_3 calculated at the MRCI level of theory, at a fixed bond length of $r = 1.2950$ Å and linear geometry.

Electronic state	Dominant electronic configuration	Calc. ΔE^a (hc cm^{-1})	Obs. T_o^b (cm^{-1})
$\tilde{X}^1\Sigma_g^+$	$\dots 1\pi_u^4 4\sigma_g^2 3\sigma_u^2$	0	...
$\tilde{a}^3\Pi_u$	$\dots 1\pi_u^4 4\sigma_g^2 3\sigma_u^1 1\pi_g^1$	17 205	16 940 ^c
$\tilde{b}^3\Pi_g$	$\dots 1\pi_u^4 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$	23 696	23 390 ^d
$^1\Pi_u$	$\dots 1\pi_u^4 4\sigma_g^2 3\sigma_u^1 1\pi_g^1$	24 997	24 675 ^e
$^3\Sigma_u^+$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$	26 120	...
$^3\Delta_u$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$	29 452	...
$^3\Sigma_u^-$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$	31 164	...
$^1\Delta_u$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$	32 123 ^f	...
$^1\Sigma_u^-$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$	32 325 ^f	...
$^1\Pi_g$	$\dots 1\pi_u^4 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$ +.. $1\pi_u^4 4\sigma_g^2 3\sigma_u^1 1\pi_g^1$	32 411	...
$^3\Sigma_g^-$	$\dots 1\pi_u^4 4\sigma_g^2 3\sigma_u^0 1\pi_g^2$ +.. $1\pi_u^4 4\sigma_g^0 3\sigma_u^2 1\pi_g^2$	34 695	...
$^1\Delta_g$	$\dots 1\pi_u^4 4\sigma_g^2 3\sigma_u^0 1\pi_g^2$ +.. $1\pi_u^4 4\sigma_g^0 3\sigma_u^2 1\pi_g^2$	42 310	42 059 ^g
$^3\Delta_u$	$\dots 1\pi_u^4 4\sigma_g^1 3\sigma_u^1 1\pi_g^2$	44 859	45 846 ^h
$^3\Sigma_u^-$	$\dots 1\pi_u^4 4\sigma_g^1 3\sigma_u^1 1\pi_g^2$	46 070	...
$^3\Pi_g$	$\dots 1\pi_u^3 4\sigma_g^2 3\sigma_u^1 1\pi_g^2$	47 335	...

^a $\Delta E = E - E(\tilde{X}^1\Sigma_g^+)$ at the given geometry, where $E(\tilde{X}^1\Sigma_g^+) = -113.8420$ E_h ($E_h \approx 4.3597 \cdot 10^{-18}$ J is the hartree); for the calculated values a (12,12) CAS and the aug-cc-pVTZ basis were used as implemented in Ref. 51, and they include the rotated frame Davidson correction.

^bVertical excitation energy.

^cReference 57.

^dReference 36.

^eReference 21.

^fStrongly perturbed levels.

^gReference 31.

^hThis work. The observed state is likely a $(0n^10)$ vibrational level of the $^3\Delta_u$ resulting in $^3\Pi_g$ vibronic symmetry (see text), where n is the odd number of bent vibrational quanta.

no direct transitions to the (000) vibrational level of either the $^3\Delta_u$ or the $^3\Sigma_u^-$ states are possible. However, transitions might be allowed by considering the direct product with the vibrational state symmetry. When odd numbers of bent vibrations are excited ($0n0$), $n = 1, 3, \dots$ both Δ_u and Σ_u^- electronic states are dipole coupled to the intermediate state through the $\Gamma_{\Pi_u} \otimes \Gamma_{\Delta_u} = \Gamma_{\Pi_g} \oplus \Gamma_{\Phi_g}$ and $\Gamma_{\Pi_u} \otimes \Gamma_{\Sigma_u^-} = \Gamma_{\Pi_g}$ symmetry product. Note that no *a priori* knowledge on the electronic symmetry of the intermediate $^3\Sigma_u^-$ state is known. Assuming the $\Gamma_{(050)} \otimes \Gamma_{el} = ^3\Sigma_u^-$ perturber state as suggested by Zhang *et al.*,⁶ the transition from $\tilde{b}^3\Pi_g$ to either Δ_u or $^3\Sigma_u^-$ is electronically allowed.

We should also mention that from a preliminary analysis of the potential energy surfaces of the excited states, we found the occurrence of several crossings in the vicinity of the $^3\Delta_u$ electronic state. It is possible that the Renner–Teller effect is quite important in this region. A more careful analysis of the rovibronic spectrum including a correct treatment of the Renner–Teller hamiltonian is clearly in place in order to have a more conclusive interpretation of the detailed structure of the final state. While such an analysis is foreseen in the forthcoming paper, we may conclude that the rough

TABLE III. Effective molecular constants for the $^3\Pi_g$ vibronic level. All values are in cm^{-1} . The origin, T , is relative to the $(0,0,0)$ $\tilde{X}^1\Sigma_g^+$ state. For comparison, constants for the two known triplet states $\tilde{a}$ and $\tilde{b}$ are reproduced from Ref. 36.

Parameter	$^3\Pi_g$ (vibronic)	$\tilde{b}^3\Pi_g$	$\tilde{a}^3\Pi_u$
T , origin	45 846.348 (3711)		
A	12.817 (1860)	13.919 (44)	13.556 (43)
B	0.41858 (176)	0.424524 (22)	0.416957 (19)
o	-0.1253 (94)	0.581 (54)	0.595 (54)
$p \times 10^3$	12.4 (32)	-2.2 (12)	-2.2 (12)

assignments from the present *ab initio* calculations and rotational analysis to be discussed in Sec. III F are correct.

F. Rotational analysis of the observed $^3\Pi_g$ state

The singlet-triplet mixing is sufficiently strong to perform UNFOLDED double-resonance experiments involving intermediate states of the $^3\Sigma_u^- (= |\psi_2\rangle)$ for $4 \leq J \leq 16$. For each accessed intermediate level J a spectrum according to Fig. 4 is obtained displaying a P, Q, and R line in accordance with the selection rules for a $\Pi \leftarrow \Sigma$ transition.

A preliminary fit⁵⁸ of the unambiguously assigned rotational structure by measuring 32 transitions in the $^3\Pi_g - ^3\Sigma_u^- (= |\psi_2\rangle)$ system yields the effective molecular constants in Table III with an average error of 0.029 cm^{-1} . The rotational constant B suggests a bond-length similar to that of the $\tilde{a}^3\Pi_u$ state. From preliminary calculations of the potential energy surfaces, we estimate that the equilibrium bond distance in the electronic $^3\Pi_g$ state should be at significantly larger values than that of the $\tilde{a}^3\Pi_u$ state. The rotational constant in the $^3\Pi_g$ state therefore would not agree with the experimentally observed value and we might rule out this state as a possible candidate for being the final $|f\rangle$ state. The spin-orbit constant A determined from the rotational spectra is non-zero. This rules out the $^3\Sigma_u^-$ state. However, note that an accurate evaluation of A requires measurements of several spin sub-states. Nevertheless, from the non-zero spin-orbit coupling constant we conclude that the observed resonances rather belong to the $^3\Delta_u$ electronic state. The Λ -type doubling parameters of $^3\Delta_u$ state are quite different compared to the known $^3\Pi$ states (Table III).

IV. CONCLUSIONS

Perturbation-facilitated-RFWM spectroscopy is a versatile technique capable of measuring topographic maps of excited triplet states of the C_3 molecule exhibiting a singlet ground state. By utilizing the nonlinear signal dependence on the mixing coefficient c_f of the intermediate state (“gate way”), it is possible to characterize transitions to final electronic states of a different spin multiplicity with respect to the initial state. The reported technique can be applied to any molecular system with states mixed by spin-orbit interaction.

The importance of the excited triplet states for the isomerization of the linear tri-carbon to an equilateral triangle structure has been pointed out by Fueno and Taniguchi³⁴ and

others.^{33,35} The lowest equilateral triplet state is expected at 1.0–1.88 eV above the linear ground state, thus it would form the lowest excited state of C_3 . This state could be formed by important radical reactions, like $\text{C} + \text{C}_2\text{H}$ and $\text{CH} + \text{C}_2$.⁵⁹

High-level *ab initio* calculations of the triplet PES as well as the perturbation facilitated dispersed LIF experiments from the newly found $^3\Pi_g$ vibronic level, which is tentatively assigned to the $^3\Delta_u$ electronic state, are under way in our laboratories. These studies shed more light on the low lying triplet manifold and will be a subject of a future report.

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