Experimental and theoretical investigation of the vibrational band structure of the $1^5\Pi_u - 1^5\Pi_g$ high-spin system of C_2

P. Bornhauser,¹ B. Visser,¹ M. Beck,¹ G. Knopp,¹ J. A. van Bokhoven,^{1,2} R. Marquardt,³ and P. P. Radi¹

¹Paul Scherrer Institute, CH-5232 Villigen, Switzerland

²Institute for Chemical and Bioengineering, ETHZ, Zürich, Switzerland

³Laboratoire de Chimie Quantique, Institut de Chimie, Université de Strasbourg 4, Rue Blaise Pascal, CS90032 67081 Strasbourg Cedex, France

(Received 22 December 2016; accepted 25 February 2017; published online 21 March 2017)

Vibrational levels of the recently observed high-spin transition ($1^5\Pi_u - 1^5\Pi_g$) of dicarbon [P. Bornhauser *et al.*, J. Chem. Phys. **142**, 094313 (2015)] are explored by applying non-linear double-resonant four-wave mixing and laser-induced fluorescence methods. The deperturbation of the $d^3\Pi_g$, $v = 8$ and $1^5\Pi_g$, $v = 3$ states results in accurate molecular constants for the $v = 3$ “dark” quintet state. In addition, the spin-orbit interaction constant is determined and parameters for the upper Swan level $d^3\Pi_g$, $v = 8$ are improved. The first excited vibrational state of $1^5\Pi_u$ is observed by performing perturbation-assisted intersystem crossing via “gateway” states in the $d^3\Pi_g$, $v = 6 \sim 1^5\Pi_g$, $v = 0$ system. The rotationally resolved spectra yield 11 transitions to $1^5\Pi_u$, $v = 1$ that include four spin-substates. Data reduction results in accurate molecular constants of this vibrational level in the shallow potential energy surface of this state. Finally, $v = 1$ and 2 of the lower quintet state ($1^5\Pi_g$) are measured by performing perturbation-assisted double-resonant excitation to the $1^5\Pi_u$, $v = 0$ state and observing dispersed fluorescence. The obtained molecular constants are compared with high level *ab initio* computations at the multi-reference configuration interaction (MRCI) level of theory by using a large correlation consistent basis set or, alternatively, by applying the computationally less demanding method of explicitly correlated multi-reference configuration interaction (MRCI-F12). The spectroscopic accuracy of both methods is evaluated by comparison with the experimental findings. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4978334>]

I. INTRODUCTION

The dicarbon radical is one of the most fundamental molecules in the universe. It is ubiquitous in hydrocarbon flames^{1–14} and carbon plasmas^{15–24} and present in several astronomical environments.^{25–27} There is experimental evidence for the role of C_2 in the early nucleation reactions to form technically important carbon nanotubes.²⁸

Theoretically, *ab initio* computations of the complex electronic structure of C_2 are highly demanding (Ref. 29 and the references therein). Many low-lying excited states that cause several avoided crossings have to be considered. The wave functions are of multireference character and near degeneracies change rapidly as a function of the nuclear distance of the two atoms. Recently, even the fundamental characteristics of bonding in dicarbon have been debated in the literature.^{30,31}

Accurate experimental observations of excited vibronic term energies offer possibilities for the comparison with high level *ab initio* potentials and are considered to be good benchmarks for improved computational methods. However, the numerous low-lying states interact and cause local perturbations in many vibrational levels, yielding complex spectra that are difficult to analyze by common spectroscopic methods.^{32–38} In this laboratory, several perturbations in the spectroscopy of C_2 have been analyzed in recent years by applying two-color resonant four-wave mixing spectroscopy

(TC-RFWM). The potential of the highly sensitive and selective method in combination with a discharge slit-jet source was initially shown by a deperturbation study of the $d^3\Pi_g$, $v = 4$ state.³⁹ The double-resonant feature of the technique yields simplified spectra by intermediate level labeling. Accurate line positions of unperturbed and perturbed transitions are unambiguously assignable. The so-called extra lines are accessible by taking advantage of the high dynamic range of the method. These weak spectral features originate from close-lying dark states that gain oscillator strength through the perturbation process. The results obtained for the $d^3\Pi_g$, $v = 4$ state solved ambiguities in the assignment of a high-resolution near infrared spectrum of the (4,8) band in the C_2 Swan system.⁴⁰ In addition, TC-RFWM spectra of the (6,5) and (6,4) bands of the Swan system ($d^3\Pi_g - a^3\Pi_u$) revealed the presence of the energetically lowest lying high-spin state ($1^5\Pi_g$) of C_2 in the vicinity of the $d^3\Pi_g$, $v = 6$ state.⁴¹ The strong interaction between $d^3\Pi_g$, $v = 6$ and $1^5\Pi_g$, $v = 0$ causes significant mixing of the wave functions of the $d^3\Pi_g$ and $1^5\Pi_g$ states and spin-forbidden dipole transitions in the (0,5) $1^5\Pi_g - a^3\Pi_u$ band system become observable. Such intersystem crossings were recently observed for $X^1\Sigma_g^+ - a^3\Pi_u$,⁴² $A^1\Pi_u - b^3\Sigma_g^-$,⁴² and for $B^1\Delta_g - a^3\Pi_u$.³⁸ These intercombination bands are important because they define accurately the relative energy between electronic states of different multiplicities. The combined experimental energy levels can

then be used to obtain a highly accurate partition function and the related thermodynamic data.⁴³ In addition, spin-forbidden transitions rationalize observed intensity distributions in the Swan band $\Delta v = 0$ sequence in the optical spectrum of Comet Hale-Bopp.²⁷

The mixed states caused by perturbations form so-called “gateway” states, i.e., rotational levels exhibiting character of both multiplicities through which population flows from one electronic state to the other. A detailed investigation of the $1^5\Pi_g, v = 0 \sim d^3\Pi_g, v = 6$ perturbation⁴¹ unraveled major features of the so-called high-pressure bands, a non-thermal emission observed in numerous experimental environments that were initially observed a century ago.⁴⁴ Recently, based on the spectroscopic characterization of the $1^5\Pi_g$ state, a perturbation-facilitated detection of the first quintet-quintet band $(0,0) 1^5\Pi_u - 1^5\Pi_g$ in C_2 has been performed by using an unfolded TC-RFWM scheme.⁴⁵ In the present study, we report on the vibrational characterization of this band by applying perturbation facilitated laser-induced fluorescence (LIF) in addition to double-resonant four-wave mixing spectroscopy.

In Section II we summarize briefly the experimental environment established for TC-RFWM and LIF. In Section III we first outline the deperturbation study (Section III A) of the $d^3\Pi_g, v = 8$ level of the Swan system. The spectroscopic characterization at high-resolution yields accurate rotational constants and the band origin for both the $d^3\Pi_g, v = 8$ and the perturbing $1^5\Pi_g, v = 3$ states. In Section III B we apply perturbation-facilitated optical-optical double-resonance (PFOODR) spectroscopy by TC-RFWM to investigate the first vibrationally excited level of the upper quintet level of the $1^5\Pi_u - 1^5\Pi_g$ electronic system. In Section III C perturbation assisted excitation of the $1^5\Pi_u, v = 0$ state is performed to observe dispersed fluorescence to the first two excited vibrational levels of the lower quintet state $1^5\Pi_g$.

II. EXPERIMENTAL

The experimental setup has been reported in recent publications^{41,45,46} and only a brief outline is given in the following. C_2 in the low-lying $a^3\Pi_u$ state was prepared in a molecular beam environment⁴⁷ by expansion of $\approx 1\%$ acetylene diluted in Ar buffer gas through a solenoid valve (General Valve, Series 9, Parker).⁴⁸ Typical backing pressures are between 5 and 11 bar. Gas pulse durations are about 750 μs . A slit-expansion geometry increases the interaction volume between the crossing area of four-wave mixing laser beams and the molecular jet.^{49,50} A pulsed applied potential difference of -800 to -900 V and $\approx 2 \mu s$ duration is actuated to the electrodes prior to the expansion zone. Trigger time-delays between the discharge and the molecular beam pulse were optimized for the maximum production of C_2 molecules which were probed by four-wave mixing ≈ 5 mm downstream of the expansion zone.

Two separately pumped dye lasers (narrowscan, Radiant Dyes) are used for TC-RFWM spectroscopy. The specified bandwidth of both laser systems is $\approx 0.04 \text{ cm}^{-1}$. A combination of optical components establishes a forward BOXCARS⁵¹ configuration.⁵² The three input beams pass along the main diagonals of a parallelepiped and cross with a small angle of ≈ 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

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

and generate the signal beam $\vec{k}_4$ along the fourth (dark) diagonal. The two laser beams of equal frequencies are usually referred to as PUMP beams $\vec{k}_1, \vec{k}_3$, and the third beam, $\vec{k}_2$, as the PROBE beam. The SIGNAL beam is collimated by an achromatic objective (FL = 1000 mm). A number of spatial and spectral filters remove scattered light and unwanted fluorescence along the ≈ 3 m propagation of the signal in

FIG. 1. Applied TC-RFWM variants. The “UP” or “hole burning” scheme shown in the left panel is applied for the deperturbation analysis of the $d^3\Pi_g, v = 8$ band. The PUMP lasers are fixed on a rovibronic transition in the $(7,6) d^3\Pi_g - a^3\Pi_u$ band. Only transitions from the common lower rotational level $|a^3\Pi_u, v = 6, J''\rangle$ are observed by scanning the PROBE laser in the wavelength region of the $(8,6)$ band. Perturbed levels in the upper state ($|\Psi_1\rangle$ and $|\Psi_2\rangle$) are mixed states of both $d^3\Pi_g$ and $1^5\Pi_g$ character. The dark state which is nominally a $1^5\Pi_g$ gains transition strength through the spin-orbit interaction and can be occasionally detected in addition to the shifted bright state (see scans in Figure 2). The right panel shows the unfolded double-resonance scheme for PFOODR studies. The PUMP lasers excite specific perturbed rotational levels in the $1^5\Pi_g, v = 0$ state that exhibit substantial quintet character (Ψ_2) from which PROBE laser scans explore rotational levels of the $1^5\Pi_u, v = 1$ state. The energy levels in the drawing are not to scale and the perturbation splittings are exaggerated. See text for details.

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 a PC for further analysis. Absolute wavelength calibration is performed for each scan step by a wavemeter (High Finesse/Ångström, WS6).

Two variants of TC-RFWM spectroscopy are exploited for the present work and depicted in Figure 1. The “UP” or “hole-burning” double-resonance scheme shown in the left panel of the figure is applied for the deperturbation study of the $v = 8$ vibrational level of the $d^3\Pi_g$ state. To obtain a signal, two resonances are addressed simultaneously in the molecule by the PUMP and PROBE lasers that share a common lower rovibronic state.

For the detection of the first vibrational state of the $1^5\Pi_u$ state, the unfolded scheme shown in the right panel of Figure 1 is applied. In this case, the common level of the two transitions is an intermediate (perturbed) level. In addition to the TC-RFWM schemes, dispersed LIF measurements to low lying vibrational levels of the $1^5\Pi_g$ state are performed by perturbation-assisted two-color excitation to the $1^5\Pi_u$, $v = 0$ state and monitoring the emission. The fluorescence is collected at right angles to both the molecular beam and laser beam propagation by a spherical aluminum mirror (diameter 60 mm, $r = 50$ mm, $f/25$). The parallel propagating LIF beam is focused onto the slit of a 1 m length monochromator (SPEX) and detected by a photo-multiplier tube.⁴⁷

III. RESULTS AND DISCUSSIONS

A. The $1^5\Pi_g$, $v = 3$ state: Deperturbation study of the $d^3\Pi_g$, $v = 8$ state

In a recent spectroscopic investigation of higher vibrational levels of C_2 , Nakajima and Endo observed perturbations in low J levels of the $d^3\Pi_g$, $v = 8$ state.⁵³ The authors suggested that the perturbation is caused by the $1^5\Pi_g$, $v = 3$ state. To characterize the interacting states in detail, we have performed a deperturbation procedure similar to the investigations reported for the $d^3\Pi_g$, $v = 4$ ³⁹ and $v = 6$ ⁴¹ levels of the Swan system. Initial measurements were performed by taking into account the spectroscopic constants for the $1^5\Pi_g$ state which have been obtained from a high-level *ab initio* computation at the multi-reference configuration interaction (MRCI) level of theory,⁵⁴ and the experimentally determined value for the vibrational origin of the $1^5\Pi_g$, $v = 0$ level of 29 258.592 2(48) cm^{-1} relative to the $a^3\Pi_u$, $v = 0$ level.⁴¹ The corresponding molecular constants for the $v = 8$ level of the $d^3\Pi_g$ state were adapted from the global analysis of the Swan system by Tanabashi *et al.*³⁶ With these constants, the origin of $1^5\Pi_g$, $v = 3$ in the vicinity of 32 115 cm^{-1} and the perturbation of the spin-sublevels F_3 $1^5\Pi_g$, $v = 3$ and F_2 $d^3\Pi_g$, $v = 8$ at $J = 5$ were correctly predicted and provided the basis for initial measurements of the deperturbation. Only small modifications of the constants were subsequently required for the final determination of the relevant molecular constants (*vide supra*).

The general implementation of the “UP” or “hole burning” scheme used for TC-RFWM spectroscopy is shown in Figure 1 (left panel). Typical examples of TC-RFWM spectra

FIG. 2. TC-RFWM spectra obtained by applying the pumping scheme shown in Figure 1 (left panel). The PUMP beams are fixed on the $R_2(4)$, $R_1(5)$, and $R_2(6)$ transitions in the (7,6) $d^3\Pi_g - a^3\Pi_u$ band for traces (a), (b), and (c), respectively. Only transitions from the common lower state ($F_2(4)$, $F_1(5)$, $F_2(6)$, respectively) are observed when scanning the PROBE laser in the wavelength region of the (8,6) band. Strong transitions in the P and R branch of the nominally $d^3\Pi_g - a^3\Pi_u$ system are observed. The lines marked with an asterisk (*) are intercombination bands ($(3,6)$ $1^5\Pi_g - a^3\Pi_u$) that gain oscillator strength through the perturbation process. The $R_2(5)$ transition in trace (b) appears due to an overlap of the PUMP frequency with $R_2(5)$ which is separated from the $R_1(5)$ by 0.07 cm^{-1} only. Please note the discontinuity of the wavenumber scale in the abscissa.

are shown in Figure 2. For these double-resonant measurements, the PUMP lasers are tuned to the $R_2(4)$, $R_1(5)$, and $R_2(6)$ transitions in the (7,6) band of the $d^3\Pi_g - a^3\Pi_u$ system at 21 375.64, 21 379.34, and 21 382.99 cm^{-1} for trace (a), (b), and (c), respectively. Rotational transitions are denoted by $^{\Delta N}\Delta J_{F'F''}(J'')$ where N is the total angular momentum, J , exclusive spin. The spin sub-levels, F_i , for a $^{2S+1}\Lambda$ state are classified by their energy ordering, i.e., F_1 for the lowest energy fine structure component and F_{2S+1} for the highest. For positive spin-orbit constants, F_1 is related to $\Omega = N - S$ and F_{2S+1} to $\Omega = N + S$. For $\Delta N = \Delta J$ and $F' = F''$ the expression is simplified to $\Delta J_{F''}(J'')$. The PROBE laser is scanned in the wavelength range of the (8,6) $d^3\Pi_g - a^3\Pi_u$ band around 22 750 cm^{-1} . The assignment of the observed transitions is straightforward owing to the strict selection rules that govern the two-photon process. Only transitions that share the same lower rotationally resolved level with the PUMP beams are observed, i.e., $F_2(4)$, $F_1(5)$, and $F_2(6)$, respectively. The transition in trace (a) at 22 732.33 cm^{-1} is the $P_2(4)$ rotational line in the (8,6) band of the $d^3\Pi_g - a^3\Pi_u$ electronic system exciting the $F_2(3)$ level of the $d^3\Pi_g$, $v = 8$ state. Analogously, the $R_2(4)$ transition exciting the $F_2(5)$ level is observed at 22 759.49 cm^{-1} . As mentioned above, a significant perturbation of $F_2(5)$ has been estimated from the initial assessment taking into account recent theoretical and experimental data. In addition to the two transitions in the P and R branches, the strong interaction causes an extra line in the vicinity of $R_2(4)$. The weak transition is marked with an asterisk (*). As predicted, the $F_2(5)$ level of the $d^3\Pi_g$, $v = 8$ state interacts with the $F_3(5)$ level of the $1^5\Pi_g$, $v = 3$ state (Figure 3) through spin-orbit interactions and off-diagonal elements of the rotational matrix [see Eq. (1) in Ref. 41]. In fact, the unperturbed $F_2(5)$ of the triplet state is an admixture of the three Ω states, $d^3\Pi_{2g}$ (22.8%), $d^3\Pi_{1g}$ (46.2%), and $d^3\Pi_{0g}$ (31.0%), because of

FIG. 3. Observed term energies of the $d^3\Pi_g, v = 8$ and the $1^5\Pi_g, v = 3$ states vs rotational quantum number J . Rotational transitions in the (8,6) band of $d^3\Pi_g - a^3\Pi_u$ are depicted in red circles. Two transitions to the perturbing state $1^5\Pi_g, v = 3$ are shown in blue. The green circles denote measured transitions in the (8,6) band from Ref. 36. The $F_3(1)$ (black) term is measured in Ref. 53. The solid lines are computed term values by taking into account the deperturbed molecular constants listed in Table IV. At the smallest possible J values for a given line, rotational interactions are negligible and levels correspond in increasing order of energy to $\Omega = -1, 0, 1, 2, 3$ for the $^5\Pi$ level, and to $\Omega = 0, 1, 2$ for the $^3\Pi$ level. See text for details.

interactions between these three fine structure components of the triplet state that result from the non-vanishing off-diagonal elements of the rotational matrix at $J = 5$. Upon perturbation via spin-orbit interaction, the triplet character is then reduced to 17.3%, 34.3%, and 22.4%, respectively, and significant quintet character is gained: $1^5\Pi_{-1g}$ (3.2%), $1^5\Pi_{0g}$ (8.0%), $1^5\Pi_{1g}$ (0.4%), $1^5\Pi_{2g}$ (5.4%), and $1^5\Pi_{3g}$ (8.9%). Among these, the $^5\Pi_{2g}$, $^5\Pi_{1g}$, and $^5\Pi_{0g}$ levels gain weight because of direct spin-orbit interaction, while the population of the $^5\Pi_{-1g}$ and $^5\Pi_{3g}$ levels is due to off-diagonal elements of the rotational matrix. As a result, the mixed $F_2(5)$ level is shifted by $+0.33\text{ cm}^{-1}$ and a weak intercombination transition $^1R_{32}(4)$ appears in the (3,6) $1^5\Pi_g - a^3\Pi_u$ band.

For trace (b) of Figure 2, the fixed laser is tuned to the $R_1(5)$ transition in the (7,6) Swan band. Again, strong P and R transitions are observed. Since the $R_2(5)$ transition is only 0.07 cm^{-1} apart from $R_1(5)$, it is excited simultaneously by the PUMP lasers. The $R_2(5)$ (8,6) $d^3\Pi_g - a^3\Pi_u$ transition observed by the PROBE in the R-branch region originates from this overlap. The weak $^0P_1(5)$ (3,6) $1^5\Pi_g - a^3\Pi_u$ is an intercombination transition (marked by the asterisk) observed due to perturbation. The $F_1(4)$ level of the $1^5\Pi_g, v = 3$ gains 15.3% triplet character (i.e., $d^3\Pi_{2g}$ (11.8%), $d^3\Pi_{1g}$ (3.1%), and $d^3\Pi_{0g}$ (0.4%)) and is, therefore, optically accessible from the $a^3\Pi_u$ state.

In trace (c), $R_2(6)$ yields the term value for $F_2(7)$, in addition the same perturbation $1^5\Pi_g, v = 3 \sim d^3\Pi_g, v = 8$ at $J = 5$ is observed as in trace (a). In this case, however, intermediate level labeling by the PUMP laser is performed by the $P_2(6)$ transition in the (7,6) $d^3\Pi_g - a^3\Pi_u$ band. The frequency of the intercombination band (*) and the shifted bright transition is measured from $J'' = 6$ and validates the data obtained in trace (a) from $J'' = 4$.

In the aforementioned analysis by Nakajima and Endo,⁵³ the molecular constants A_v and o_v of the 5, 7, and 10 levels of the $d^3\Pi_g$ state were adjusted from the values of the most recent updated molecular constants for the C_2 Swan system.⁵⁵ The determined constants are more reliable because many branches between different spin sublevels in the upper and lower states

were observed in the spectra of the $d^3\Pi_g - c^3\Sigma_u^+$ system. In contrast, intensities of rotational branches between different spin sublevels for the Swan bands ($d^3\Pi_g - a^3\Pi_u$) are generally too weak to be observed, especially for higher vibrational levels. The o_v for $v = 5, 7$, and 10 from the experiment of Nakajima and Endo are in close agreement with the values obtained by the global analysis of the Swan band by Tanabashi *et al.*³⁶ As a consequence, the molecular constants for $d^3\Pi_g, v = 8$ from the latter work have been adapted for this deperturbation study.

Table I lists the assignments of 44 observed transitions (column 2) and the corresponding upper rotational levels. In addition to well resolved P and R branch transitions in the (8,6) band of the $d^3\Pi_g - a^3\Pi_u$ Swan system, three intercombination transitions are measured. The inclusion of such extra lines is essential since they were found to yield significantly improved B and λ parameters of the perturbing vibronic state.³⁹ A first least-squares optimization procedure to the transitions listed in Table I by the PGOPHER software⁵⁶ has been performed. The details of the procedure and the Hamiltonian for the linear molecule are given in a preceding publication.⁴¹ The root mean square value for the reduction is 0.015 cm^{-1} , which is approximately half of the specified laser bandwidth of the dye lasers. In addition to the determined constants of the perturbing $1^5\Pi_g, v = 3$ state, the origin, T and spin-spin λ constants of $d^3\Pi_g, v = 8$ were refined from the original values given by Tanabashi *et al.*³⁶ In contrast to this work, the authors have reduced data from the higher J values only and omitted the low J transitions owing to the perturbation.

Moreover, taking into account the results of our data reduction, numerous transitions in the (8,6) band of the Swan system measured by Tanabashi *et al.*³⁶ between $J = 7-19$ are assignable and can be included in the analysis to obtain more accurate molecular constants. 48 transitions designated by the authors as well resolved isolated lines and, in addition, the two strongly perturbed transitions $R_3(6)$ and $P_3(8)$ were combined with our data set. The transitions are listed in Table II and display a systematic shift of $+0.036\text{ cm}^{-1}$ relative to our measurements. The magnitude of the shift is in close agreement with the reported correction in the report of Tanabashi *et al.*⁵⁷ on the $4051.6\text{ \AA}$ band of C_3 relative to the measurements of the Saykally group⁵⁸ which are in accordance with our observations of the same band.⁴⁶ For consistency with the dataset of Tanabashi *et al.*, the measured transitions listed in Table I are shifted accordingly.

Additional information is available by considering the aforementioned measurements on the (8,5) $d^3\Pi_g - c^3\Sigma_u^+$ band by Nakajima and Endo.⁵³ In contrast to $^3\Pi - ^3\Pi$ transitions, this electronic system yields accurate absolute values for the constants A_v and o_v of the $d^3\Pi_g$ state. Furthermore, the work reports the $F_3(1)$ term value which is missing in our data. 28 transitions in the (8,5) band have been reported in the range of $J = 1-5$. Three transitions ($R_{31}(2)$, $Q_{32}(3)$, and $R_{33}(2)$) are omitted owing to erroneous assignment. In fact, the authors assigned the lines to perturbed transitions displaying perturbation shifts on the order of $\approx 1\text{ cm}^{-1}$. However, our observations of this perturbed level ($F_3(3)$) in the $d^3\Pi_g, v = 8$ state yield a significantly lower shift of $\approx 0.17\text{ cm}^{-1}$. Apart from $F_3(3)$, the relative values of the listed perturbations in Table III are in agreement with the energy level shifts displayed in Figure 4 of

TABLE I. TC-RFWM transitions measured in the wavenumber range of the perturbed (8,6) $d^3\Pi_g - a^3\Pi_u$ band. The common lower level is labeled by the PUMP transition (third column). The upper level and the assignments of the PROBE transitions are given in column one and two. Three intercombination bands are measured and labeled as (1-a) in the second column denoting the (3,6) $1^5\Pi_g - a^3\Pi_u$ band. For consistency with the calibration of Tanabashi *et al.*³⁶ the wavenumbers are shifted by $+0.036\text{ cm}^{-1}$. Observed transitions and residuals are given in cm^{-1} .

Upper level	Assignment	Pump	Observed	Residuals	Perturbation
F1e(2)	Q1(2) (8,6) d-a	(7,6)R1(2)	22 747.51	-0.01	-0.03
F1f(3)	P1(4) (8,6) d-a	(7,6)R1(4)	22 736.69	0.02	-0.02
F1f(3)	R1(2) (8,6) d-a	(7,6)R1(2)	22 755.21	0.00	-0.04
F1e(4)	P1(5) (8,6) d-a	(7,6)R1(5)	22 733.79	0.00	0.06
F1e(4)	R1(3) (8,6) d-a	(7,6)R1(3)	22 757.82	0.01	0.07
F1f(5)	P1(6) (8,6) d-a	(7,6)R1(6)	22 730.65	0.01	-0.04
F1f(5)	R1(4) (8,6) d-a	(7,6)R1(4)	22 760.30	0.01	-0.03
F1e(6)	R1(5) (8,6) d-a	(7,6)R1(5)	22 762.85	0.01	-0.11
F1e(6)	R1(5) (8,6) d-a	(7,6)R2(5)	22 762.86	0.02	-0.11
F1f(7)	R1(6) (8,6) d-a	(7,6)R1(6)	22 765.87	-0.01	0.20
F1f(7)	R1(6) (8,6) d-a	(7,6)R2(6)	22 765.89	0.01	0.22
F1e(8)	R1(7) (8,6) d-a	(7,6)R1(7)	22 768.51	0.00	0.06
F1f(9)	R1(8) (8,6) d-a	(7,6)R1(8)	22 771.32	0.04	0.07
F1e(10)	R1(9) (8,6) d-a	(7,6)R1(9)	22 774.19	0.00	0.04
F1e(10)	R1(9) (8,6) d-a	(7,6)P1(9)	22 774.20	0.01	0.05
F2f(1)	P2(2) (8,6) d-a	(7,6)R2(2)	22 738.07	-0.01	-0.12
F2e(2)	P2(3) (8,6) d-a	(7,6)R2(3)	22 735.03	0.00	-0.23
F2f(3)	P2(4) (8,6) d-a	(7,6)R2(4)	22 732.33	-0.01	0.18
F2f(3)	R2(2) (8,6) d-a	(7,6)R2(2)	22 753.11	0.00	0.19
F2e(4)	R2(3) (8,6) d-a	(7,6)R2(3)	22 755.96	0.00	-0.01
F2f(5)	P2(6) (8,6) d-a	(7,6)R2(6)	22 726.45	-0.01	0.33
F2f(5)	R2(4) (8,6) d-a	(7,6)R2(4)	22 759.49	-0.01	0.33
F2e(6)	R2(5) (8,6) d-a	(7,6)R1(5)	22 762.40	0.01	0.07
F2e(6)	R2(5) (8,6) d-a	(7,6)R2(5)	22 762.38	-0.01	0.05
F2f(7)	R2(6) (8,6) d-a	(7,6)R2(6)	22 765.52	0.00	0.02
F2e(8)	R2(7) (8,6) d-a	(7,6)R2(7)	22 768.62	0.01	-0.08
F3e(2)	P3(3) (8,6) d-a	(7,6)P3(3)	22 731.51	0.00	0.20
F3f(3)	P3(4) (8,6) d-a	(7,6)R3(4)	22 728.12	-0.03	0.17
F3f(3)	P3(4) (8,6) d-a	(7,6)P3(4)	22 728.10	-0.05	0.15
F3f(3)	R3(2) (8,6) d-a	(7,6)R3(2)	22 752.81	-0.01	0.19
F3f(3)	R3(2) (8,6) d-a	(7,6)P3(2)	22 752.78	-0.04	0.16
F3e(4)	P3(5) (8,6) d-a	(7,6)P3(5)	22 725.16	-0.01	0.03
F3e(4)	P3(5) (8,6) d-a	(7,6)R3(5)	22 725.16	0.00	0.04
F3e(4)	R3(3) (8,6) d-a	(7,6)P3(3)	22 756.65	0.01	0.05
F3f(5)	P3(6) (8,6) d-a	(7,6)R3(6)	22 721.82	-0.03	-0.08
F3f(5)	R3(4) (8,6) d-a	(7,6)P3(4)	22 759.65	-0.04	-0.09
F3e(6)	R3(5) (8,6) d-a	(7,6)P3(5)	22 763.32	0.02	-0.19
F3e(6)	R3(5) (8,6) d-a	(7,6)R3(5)	22 763.32	0.02	-0.19
F3f(7)	R3(6) (8,6) d-a	(7,6)R3(6)	22 766.76	0.00	0.20
F3f(7)	R3(6) (8,6) d-a	(7,6)P3(6)	22 766.76	0.00	0.20
F3e(8)	R3(7) (8,6) d-a	(7,6)P3(7)	22 770.28	0.01	0.11
F1e(4)	oP1(5) (3,6) 1-a	(7,6)R1(5)	22 733.08	-0.01	-0.12
F3f(5)	rR32(4) (3,6) 1-a	(7,6)R2(4)	22 758.20	0.01	-0.32
F3f(5)	pP32(6) (3,6) 1-a	(7,6)R2(6)	22 725.14	0.00	-0.34

the report of Nakajima and Endo.⁵³ But absolute values differ due to the augmented molecular constants T , λ , and o of the $d^3\Pi_g$, $v = 8$ state. As a consequence, the rotational level $F_1(4)$ has to be considered as perturbed by 0.055 cm^{-1} in contrast to the findings of Nakajima and Endo.⁵³

Similar to the considerations above, the inclusion of the remaining 25 transitions of Nakajima and Endo (Table III) yields a shift of $+0.020\text{ cm}^{-1}$ relative to our measurements. The deviation is computed by taking into account the preliminary

perturbation analysis above and the reported values for $c^3\Sigma_u^+$, $v = 5$.⁵⁹ To be consistent with the calibration of Tanabashi *et al.*, the transitions have been modified by $+0.016\text{ cm}^{-1}$ by taking into account the systematic shift of our results as discussed above.

Table IV lists the molecular constants including the perturbation parameters that are obtained by performing a global least-squares optimization procedure on the transitions listed in Tables I–III by using PGOPHER.⁵⁶ Weighting factors of 0.020,

TABLE II. Selected transitions measured in Ref. 36 in the (8,6) $d^3\Pi_g - a^3\Pi_u$ band. The upper level and the assignments are given in column one and two, respectively. Observed transitions and residuals are given in cm^{-1} . See text for details.

Upper level	Assignment	Observed	Residuals	Perturbation
F1e(8)	P1(9) (8,6) d-a	22 721.58	0.00	0.06
F1f(9)	P1(10) (8,6) d-a	22 718.50	0.03	0.06
F1f(9)	R1(8) (8,6) d-a	22 771.30	0.01	0.04
F1e(10)	P1(11) (8,6) d-a	22 715.41	-0.04	0.00
F1e(10)	R1(9) (8,6) d-a	22 774.16	-0.03	0.01
F1f(11)	P1(12) (8,6) d-a	22 712.39	0.04	0.05
F1f(11)	R1(10) (8,6) d-a	22 777.08	0.04	0.06
F1f(13)	P1(14) (8,6) d-a	22 706.26	0.00	0.00
F1f(13)	R1(12) (8,6) d-a	22 782.94	0.04	0.05
F1e(14)	P1(15) (8,6) d-a	22 703.41	0.00	0.14
F1e(14)	R1(13) (8,6) d-a	22 786.06	-0.01	0.13
F1f(15)	P1(16) (8,6) d-a	22 700.28	0.06	0.08
F1f(15)	R1(14) (8,6) d-a	22 788.89	0.04	0.05
F1f(17)	P1(18) (8,6) d-a	22 694.22	0.05	0.06
F1f(19)	P1(20) (8,6) d-a	22 688.17	0.05	0.05
F1f(19)	R1(18) (8,6) d-a	22 800.81	0.00	0.01
F2f(9)	P2(10) (8,6) d-a	22 714.20	-0.02	0.01
F2f(9)	R2(8) (8,6) d-a	22 771.84	-0.02	0.01
F2e(10)	P2(11) (8,6) d-a	22 711.36	0.02	0.03
F2e(10)	R2(9) (8,6) d-a	22 775.05	0.01	0.03
F2f(11)	P2(12) (8,6) d-a	22 708.24	-0.02	-0.01
F2f(11)	R2(10) (8,6) d-a	22 778.09	-0.03	-0.03
F2e(12)	P2(13) (8,6) d-a	22 705.45	0.06	0.05
F2e(12)	R2(11) (8,6) d-a	22 781.31	0.01	0.00
F2f(13)	P2(14) (8,6) d-a	22 702.32	-0.05	0.00
F2f(13)	R2(12) (8,6) d-a	22 784.39	-0.04	0.01
F2e(14)	P2(15) (8,6) d-a	22 699.54	0.05	0.07
F2e(14)	R2(13) (8,6) d-a	22 787.55	-0.02	0.00
F2e(16)	P2(17) (8,6) d-a	22 693.57	0.04	0.05
F2e(16)	R2(15) (8,6) d-a	22 793.80	0.03	0.04
F2e(18)	P2(19) (8,6) d-a	22 687.61	0.03	0.03
F2e(18)	R2(17) (8,6) d-a	22 799.94	0.02	0.02
F3f(7)	P3(8) (8,6) d-a	22 716.15	-0.03	0.17
F3f(7)	R3(6) (8,6) d-a	22 766.75	0.00	0.20
F3e(8)	P3(9) (8,6) d-a	22 713.32	0.00	0.09
F3e(8)	R3(7) (8,6) d-a	22 770.25	-0.01	0.08
F3f(9)	P3(10) (8,6) d-a	22 710.13	-0.01	0.04
F3f(9)	R3(8) (8,6) d-a	22 773.21	-0.02	0.04
F3e(10)	P3(11) (8,6) d-a	22 707.36	-0.03	0.01
F3e(10)	R3(9) (8,6) d-a	22 776.70	-0.04	0.00
F3f(11)	P3(12) (8,6) d-a	22 704.23	-0.01	0.02
F3f(11)	R3(10) (8,6) d-a	22 779.64	-0.05	-0.02
F3e(12)	P3(13) (8,6) d-a	22 701.46	-0.03	0.00
F3e(12)	R3(11) (8,6) d-a	22 783.11	-0.04	-0.01
F3f(13)	P3(14) (8,6) d-a	22 698.36	0.00	0.02
F3f(13)	R3(12) (8,6) d-a	22 786.06	-0.01	0.01
F3f(15)	P3(16) (8,6) d-a	22 692.46	0.00	0.01
F3f(15)	R3(14) (8,6) d-a	22 792.38	-0.01	0.00
F3f(17)	P3(18) (8,6) d-a	22 686.54	-0.01	0.00
F3f(17)	R3(16) (8,6) d-a	22 798.67	0.02	0.03

0.050, and 0.010 have been introduced for the data sets, respectively.

As mentioned above, the molecular constants, A_v and σ_v , for $v = 5, 7$, and 10 were modified by Nakajima and Endo⁵³ from the most recent update of the molecular constants of the Swan band.⁵⁵ In a similar manner, our data reduction is

improved by lowering the σ_8 constant whereas no modification is required for A_8 . All other molecular constants for the $d^3\Pi_g$, $v = 8$ state not listed in Table IV and all constants for a $^3\Pi_u$, $v = 6$ were kept fixed to the values of Ref. 36. Similarly, the molecular constants for $c^3\Sigma_u^+$, $v = 5$ were adapted from Ref. 53. An excellent agreement between the observed and simulated

TABLE III. Selected transitions in the (8,5) band of the $d^3\Pi_g - c^3\Sigma_u^+$ system measured by Ref. 53. The upper level and the assignments are given in column one and two, respectively. For consistency with the calibration of Tanabashi *et al.*,³⁶ a shift of $+0.016\text{ cm}^{-1}$ is applied to the wavenumbers. Observed transitions and residuals are given in cm^{-1} . See text for details.

Upper level	Assignment	Observed	Residuals	Perturbation
F1e(2)	Q1(2) (8,5) d-c	13 569.80	-0.01	-0.04
F1e(2)	qR12(1) (8,5) d-c	13 570.06	-0.01	-0.04
F1f(3)	P1(4) (8,5) d-c	13 559.21	0.01	-0.03
F1f(3)	pQ12(3) (8,5) d-c	13 559.48	0.00	-0.04
F1f(3)	R1(2) (8,5) d-c	13 577.50	-0.01	-0.05
F1e(4)	Q1(4) (8,5) d-c	13 569.70	-0.01	0.06
F1e(4)	qR12(3) (8,5) d-c	13 569.98	-0.01	0.05
F1f(5)	R1(4) (8,5) d-c	13 582.80	-0.01	-0.05
F1f(5)	pR13(4) (8,5) d-c	13 549.81	0.00	-0.05
F2f(1)	qP21(2) (8,5) d-c	13 581.95	-0.01	-0.12
F2f(1)	oP23(2) (8,5) d-c	13 563.52	-0.01	-0.11
F2f(1)	Q2(1) (8,5) d-c	13 582.21	-0.01	-0.12
F2f(1)	qR23(0) (8,5) d-c	13 581.54	-0.01	-0.12
F2e(2)	rQ21(2) (8,5) d-c	13 587.58	0.00	-0.23
F2e(2)	pQ23(2) (8,5) d-c	13 569.15	0.01	-0.22
F2e(2)	R2(1) (8,5) d-c	13 587.84	0.00	-0.23
F2f(3)	qP21(4) (8,5) d-c	13 578.68	0.01	0.19
F2f(3)	Q2(3) (8,5) d-c	13 578.97	0.01	0.19
F2f(3)	sR21(2) (8,5) d-c	13 597.00	0.01	0.20
F2f(3)	qR23(2) (8,5) d-c	13 578.57	0.02	0.21
F3f(1)	rP31(2) (8,5) d-c	13 596.14	0.01	-0.06
F3f(1)	rQ32(1) (8,5) d-c	13 596.40	0.01	-0.06
F3e(2)	sQ31(2) (8,5) d-c	13 602.97	0.00	0.19
F3e(2)	sR32(1) (8,5) d-c	13 603.24	0.01	0.20
F3e(2)	Q3(2) (8,5) d-c	13 584.54	0.00	0.19

transitions is obtained. The root mean square value of the data reduction is 0.021 cm^{-1} .

Term energies of the upper rotational states are depicted in Figure 3 (red circles). A value of $1.53J(J+1)\text{ cm}^{-1}$ has been subtracted from the energies in order to display the significant

parts of the vibronic levels and their crossings. The solid lines are computed by PGOPHER⁵⁶ adopting the molecular constants listed in Table IV. Qualitatively, the same pattern is observed as for the $1^5\Pi_g, v=0 \sim d^3\Pi_g, v=6$ perturbation.⁴¹ The three spin-substates of the d state are affected by the five F-levels of

FIG. 4. Observation of the $1^5\Pi_u, v=1$ state by applying PFOODR spectroscopy. The unfolded TC-RFWM scheme shown in Figure 1 (right panel) is utilized by exciting the perturbed Ψ_2 level exhibiting substantial quintet character from the initial $a^3\Pi_u, v=5$ state. For traces (a) and (b), the $rR_{21}(4)$ transition at $21\,414.06\text{ cm}^{-1}$ labels the $F_2(5)$ state in the nominally $1^5\Pi_g, v=0$ state. From this intermediate state, the $R_2(5)$ and $P_2(5)$ transitions to $F_2(6)$ and $F_2(4)$ of $1^5\Pi_u, v=1$ are observed and shown in traces (a) and (b), respectively. For traces (c) and (d), the transition $sR_{42}(4)(0,5) 1^5\Pi_g - a^3\Pi_u$ at $21\,418.85\text{ cm}^{-1}$ is used to label $F_4(5)$. Again, two transitions in the R and P branch are observed, respectively, and determine the term energies $F_4(6)$ and $F_4(4)$ of $1^5\Pi_u, v=1$. The solid lines are Gaussian least-squares fits to obtain accurate line-center positions (see text for details).

TABLE IV. Optimized molecular constants (in cm^{-1}) for the $1^5\Pi_g, v = 3$ and the $d^3\Pi_g, v = 8$ states. In addition, the spin-orbit coupling constant for the perturbation is listed. All values are in cm^{-1} . The origin, T , is relative to the $a^3\Pi_u, v = 0$ level. Numbers in parenthesis are one standard deviation. See text for details.

State	Parameter	Value	Reference ^a
$1^5\Pi_g, v = 3$	T	32 113.974(10)	
	B	1.095 84(37)	
	$D \times 10^6$	6.3(fixed) ^b	
	A	9.055 1(86)	
$d^3\Pi_g, v = 8$	T	32 102.641 7(13)	32 102.671 3(90)
	λ	0.094 3(20)	0.046(12)
	o	0.466 8(29)	0.491 5(96)
$\langle d^3\Pi_1, v = 8 H_{so} 1^5\Pi_1, v = 3 \rangle$		1.073(7)	

^aReference 36.

^bComputed *ab initio* value (Section III D).

the quintet. Strong perturbations occur at rotational quantum numbers close to a term energy curve crossing. One observed intercombination transition occurs at $J = 4$ where the two F_1 curves interact. The second measurement of a dark state is made possible by the close interaction of the triplet $F_2(5)$ term with $F_3(5)$ of the quintet state (blue circles).

Considering the molecular constants listed in Table IV for $1^5\Pi_g, v = 3$ and the values for the ground vibrational level $v = 0$,⁴¹ an extrapolation of the perturbing state to $v = 6$ is possible. The term energies suggest a perturbation with $d^3\Pi_g, v = 10$ in the proximity of $J = 20$. In fact, a careful inspection of the reported transitions by Tanabashi *et al.*³⁶ in the (10,9) $d^3\Pi_g - a^3\Pi_u$ Swan band reveals the expected perturbation pattern for a quintet $\sim$ triplet interaction. A preliminary deperturbation analysis in analogy to the $1^5\Pi_g, v = 3 \sim d^3\Pi_g, v = 8$ system outlined above yields the constants ν_6 and B_6 for $1^5\Pi_g, v = 6$ listed in Table VIII. However, in contrast to the deperturbation analysis for $v = 0$ ⁴¹ and $v = 3$ in this work, these values are considered as preliminary because no extra lines to the perturbing state have been reported. Such extra lines are necessary to obtain accurate molecular constants for the perturber (*vide supra*). Nevertheless, by taking into account the limited accuracy, an estimate of the equilibrium parameters ω_e and $\omega_e x_e$ is obtained and listed in Table VIII.

The spin-orbit interaction constant, $A(d^3\Pi_g, 1^5\Pi_g)$, can be estimated from the fitted perturbation matrix elements $\langle d^3\Pi_1, v_i | H_{so} | 1^5\Pi_1, v_j \rangle$ divided by the vibrational overlap integral $\langle v_i | v_j \rangle$. The latter is evaluated from the potential energy curves computed by *ab initio* methods outlined in Sec. III D and applying the LEVEL program from Le Roy.⁶⁰

The results are listed in Table V. The spin-orbit interaction parameters are not constant due to uncertainties in the experimental determination of the matrix elements and inaccuracies of the overlap integrals. However, the deviations from the mean value $10.97(43) \text{ cm}^{-1}$ are less than 7%. The spin-orbit interaction constant $A(d^3\Pi_g, 1^5\Pi_g)$ is close to the mean absolute value of the individual spin-orbit constants of the $d^3\Pi_g$ and $1^5\Pi_g$ states ($\approx 14 \text{ cm}^{-1}$ and $\approx 9 \text{ cm}^{-1}$, respectively).

B. The $1^5\Pi_u, v = 1$ state: A PFOODR study

The spectroscopic characterization of the first vibrational level of the $1^5\Pi_u$ state is based on the recent PFOODR study that allowed the first observation of a high-spin transition in C_2 , i.e., the origin band of the $1^5\Pi_u - 1^5\Pi_g$ system.⁴⁵

The energy scheme shown in Figure 1 (right panel) depicts the implementation of TC-RFWM for the rotational characterization of the first vibrationally excited state of the $1^5\Pi_u$ state. Traces (a) and (b) in Figure 4 display scans from the common intermediate level $F_2(5) = |\Psi_2\rangle$. This nominally $1^5\Pi_g, v = 0$ level gains 26.2% triplet character from the perturbation process (i.e., $d^3\Pi_{2g}$ (18.2%), $d^3\Pi_{1g}$ (7.3%), and $d^3\Pi_{0g}$ (0.7%)) and is therefore accessible from the thermally populated $a^3\Pi_u, v = 5$ state. The $|\Psi_2\rangle$ gateway state is excited by fixing the PUMP lasers on the rovibronic $^1R_{21}(4)$ transition in the (0,5) $1^5\Pi_g - a^3\Pi_u$ intercombination band. Traces (a) and (b) show the PROBE scans performed to observe the $R_2(5)$ and $P_2(5)$ transitions to the $1^5\Pi_u, v = 1$ state which determine the term energies of $J = 6$ and 4 in the F_2 manifold. Likewise, PROBE scans of the $P_4(5)$ and $R_4(5)$ transitions originating from the intermediate state $F_4(5)$ are shown in the figure by traces (c)

TABLE V. Spin orbit interaction constant between the $d^3\Pi_g$ and $1^5\Pi_g$ states. The overlap integral $\langle v_i | v_j \rangle$ is obtained by applying the LEVEL software program from Le Roy⁶⁰ and taking into account the *ab initio* results outlined in Section III D. See text for details.

Perturbation	Value	$\langle v_i v_j \rangle$	$A(d^3\Pi_g, 1^5\Pi_g)$
$\langle d^3\Pi_1, v = 6 H_{so} 1^5\Pi_1, v = 0 \rangle$	4.6220(88) ^a	0.420	11.00(2)
$\langle d^3\Pi_1, v = 8 H_{so} 1^5\Pi_1, v = 3 \rangle$	1.073(7) ^b	0.0917	11.70(8)
$\langle d^3\Pi_1, v = 10 H_{so} 1^5\Pi_1, v = 6 \rangle$	1.990(27) ^c	0.195	10.21(14)

^aReference 41.

^bThis work.

^cPreliminary result (see text).

TABLE VI. PFOODR transitions by TC-RFWM. The initial transition (fourth column) occurs in the intersystem band $(0,5) 1^5\Pi_g - a^3\Pi_u$ to a “gateway” state (third column) exhibiting substantial quintet character. The final state (first column) is the rotational level of the first vibrational quanta in $1^5\Pi_u$. The rovibronic transitions are listed in the second column. Transitions and residuals are in cm^{-1} . See text for details.

Upper level $1^5\Pi_u, v=1$	Assignment $1^5\Pi_u - 1^5\Pi_g$	Common intermediate level $1^5\Pi_g, v=0$	Pump $1^5\Pi_g - a^3\Pi_u$	Observed	Residuals
F2e(3)	(1,0)pP2e(4)	F2e(4)	(0,5)rR21(3)	22 606.60	-0.02
F2f(4)	(1,0)pP2f(5)	F2f(5)	(0,5)rR21(4)	22 608.22	-0.01
F2e(5)	(1,0)rR2e(4)	F2e(4)	(0,5)rR21(3)	22 622.44	0.00
F2f(6)	(1,0)rR2f(5)	F2f(5)	(0,5)rR21(4)	22 628.76	0.01
F3e(1)	(1,0)qP3e(2)	F3e(2)	(0,5)qP32(3)	22 611.36	0.04
F3f(4)	(1,0)pP3f(5)	F3f(5)	(0,5)rR32(4)	22 604.37	0.02
F3f(6)	(1,0)rR3f(5)	F3f(5)	(0,5)rR32(4)	22 628.85	0.01
F4f(4)	(1,0)pP4f(5)	F4f(5)	(0,5)sR42(4)	22 601.56	-0.01
F4f(6)	(1,0)rR4f(5)	F4f(5)	(0,5)sR42(4)	22 631.43	0.01
F5e(3)	(1,0)pP5e(4)	F5e(4)	(0,5)sR53(3)	22 601.24	-0.02
F5e(5)	(1,0)rR5e(4)	F5e(4)	(0,5)sR53(3)	22 631.86	-0.01

and (d). This gateway state exhibits 18.7% triplet character (i.e., $d^3\Pi_{2g}$ (1.6%), $d^3\Pi_{1g}$ (7.3%), and $d^3\Pi_{0g}$ (9.8%)). F₄(5) is excited in the $(0,5) 1^5\Pi_g - a^3\Pi_u$ band by $sR_{42}(4)$. The two transitions observed to the final state in the R and P branch measure accurately the $J=6$ and 4 rotational levels of the $1^5\Pi_u$, $v=1$ level. In comparison to the origin band, a significantly reduced signal-to-noise ratio is observed for the $(1,0) 1^5\Pi_u - 1^5\Pi_g$ band. Therefore, in contrast to the $(0,0)$ band, no Q-band transitions have been detected. Nevertheless, the sensitivity of TC-RFWM has been sufficient to observe 11 transitions in four spin sub-bands that accurately determine the molecular constants of the first excited vibrational state of $1^5\Pi_u$. The measured transitions are listed in Table VI. A conventional Hamiltonian for a linear molecule is used to perform a non-linear least squares fit to obtain molecular parameters (PGOPHER⁵⁶). The matrix elements utilized are detailed in Ref. 45. An excellent agreement between the observed transitions and the simulation is obtained. The root mean square value for the data reduction is 0.02 cm^{-1} which is approximately half of the specified bandwidth of the lasers. The optimized molecular constants for the $1^5\Pi_u$, $v=1$ state are listed in Table VII in addition to the respective constants for $v=0$.⁴¹

The excited state vibrational energy $\Delta G_{1/2}$ of $823.435(15) \text{ cm}^{-1}$ is in good agreement with the *ab initio*

computations (*vide supra*) and corroborates the initial assignment of the $(0,0) 1^5\Pi_u - 1^5\Pi_g$ transition in Ref. 45. Attempts to observe a further vibrational level in the $1^5\Pi_u$ state were unsuccessful. The $v=2$ level is computed at $\approx 1580 \text{ cm}^{-1}$ above the vibrationless level, which is close to the dissociation threshold of the shallow potential.⁴⁵

C. Vibrational origins of the $1^5\Pi_g$, $v=1$ and $v=2$ states: PFOODR and LIF study

The spectroscopic analysis of the substantial perturbations in the $v=6$ and $v=8$ levels of the upper Swan state $d^3\Pi_g$ revealed the vibrational ground level of the quintet state ($1^5\Pi_g$, $v=0$)⁴¹ and the third quanta ($1^5\Pi_g$, $v=3$) as reported in Section III A above, respectively. Taking into account vibrational frequencies of the $d^3\Pi_g$ and $1^5\Pi_g$ states, no further significant perturbations between close lying vibrational levels in the two states are expected that are accessible from thermally populated rotational levels in the $a^3\Pi_u$ state. However, by taking into account the recent characterization of the $(0,0) 1^5\Pi_u - 1^5\Pi_g$ origin band,⁴⁵ double-resonant pathways to rotational energy levels of the $1^5\Pi_u$, $v=0$ have been established. By accessing the upper quintet state, optically allowed transitions to vibrational levels of $1^5\Pi_g$ occur and are accessible by performing LIF measurements. In the following, we report on the characterization of $v=1$ and 2 of the $1^5\Pi_g$ state. In a first step intersystem crossing to the upper quintet state $1^5\Pi_u$ is performed by a two-photon transition through a perturbed level in the $d^3\Pi_g$, $v=6 \sim 1^5\Pi_g$, $v=0$ system. In the second step, dispersed fluorescence from $1^5\Pi_u$, $v=0$ is observed and analyzed.

PFOODR excitation is performed by populating the F₂(5) “gateway” utilizing the $rR_{21}(4)$ rovibronic transition at $21\,414.06 \text{ cm}^{-1}$ ($h\nu_1$) in the $(0,5) 1^5\Pi_g - a^3\Pi_u$ band. The same intermediate level exhibiting 26.2% triplet character has been used to characterize the first excited vibrational quanta, $v=1$, of $1^5\Pi_u$ (Section III B). The second laser ($h\nu_2$) is tuned to P₂(5) $(0,0) 1^5\Pi_u - 1^5\Pi_g$ and populates the final level F₂(4) of $1^5\Pi_u$, $v=0$. Dispersed fluorescence measurements upon

TABLE VII. Optimized molecular constants of the $1^5\Pi_u$, $v=1$ state. For comparison, parameters for the $v=0$ state are listed in addition. All values are given in cm^{-1} . T is relative to the $a^3\Pi_u$, $v=0$ state. Uncertainties are one standard deviation.

State	Parameter	$v=1$	$v=0^a$
	T	51 873.235(14)	51 049.799 5(48)
	B	1.165 88(46)	1.219 05(21)
	A	8.091(18)	8.198 3(37)
	λ	0.025 2(45)	0.035 0(15)
	o	-0.044 1(59)	-0.034 3(19)
	$D \times 10^6$	...	-10(1)

^aReference 41.

FIG. 5. ON/OFF dispersed fluorescence from the $1^5\Pi_u$, $v = 0$ level excited by applying PFOODR. The abscissa is the wavenumber shift from the exciting $P_2(5)$ line in the $(0,0)$ $1^5\Pi_u - 1^5\Pi_g$ band. The red (dotted) trace is observed by turning $h\nu_2$ OFF. LIF from both lasers ON is shown in blue (solid). The intensity of both traces is offset below -500 cm^{-1} for clarity. The difference spectrum (green, solid) displays the vibrational progression with $v = 1$ and 2. Shown inverted is a simulation by taking into account the vibrational frequencies obtained by the *ab initio* computations discussed in Section III D. See text for details.

excitation are shown in Figure 5. The spectrum is plotted as a function of relative wave number, given as the shift from the excitation $P_2(5)$ wavenumber.

In addition to fluorescence from $1^5\Pi_u$, $v = 0$ other emission processes have to be taken into account. While $h\nu_2$ yields negligible emission, significant fluorescence is induced by one-photon excitation of the intermediate “gateway” state $h\nu_1$. From the partial triplet character of the $1^5\Pi_g$, $F_2(5)$ level emission is observed to lower lying vibrational levels of the $a^3\Pi_u$ state. Since substantial perturbation-facilitated population transfer to the $F_1(5)$ of the $d^3\Pi_g$, $v = 6$ state is occurring (*vide supra*), additional fluorescence is generated in the (6,6) and (6,7) Swan band and observed in the spectral region shown in Figure 5. This transfer process produces enhanced emission from $v = 6$ with respect to other vibrational levels.⁴¹ In addition, unspecified molecules like the anionic C_2^{-48} that are generated in the discharge source have to be considered as further sources for observed fluorescence. As a consequence, DLIF scans are the result of successive ON/OFF measurements, which clearly identify emissions not resulting from both input photons. The red trace (dotted) is observed when the laser photon $h\nu_2$ is OFF. In contrast, the blue trace (solid) is measured with both lasers ON.

The difference spectrum (green, solid) shows clearly two transitions that are assigned to the vibrational progression in the lower quintet state, i.e., (0,1) and (0,2) of the $1^5\Pi_u - 1^5\Pi_g$ electronic system. The spectrum shown inverted is a simulation performed using the computed *ab initio* results, which are discussed in Section III D. The short progression observed is expected for two states of comparable equilibrium distances, i.e., 1.56 and 1.51 Å for $1^5\Pi_g$ and $1^5\Pi_u$, respectively (see Table VIII below). In fact, the computed Franck-Condon factors for (0,0), (0,1), and (0,2)

bands are 0.83, 0.13, and 0.04, respectively, which is in close agreement with the intensity distribution observed in Figure 5. Gaussian fits to the ON/OFF spectrum in Figure 5 have been performed for the determination of the line centers which are listed in Table VIII including the estimated errors.

The dispersed LIF measurements utilizing the 1 m spectrometer provide only limited resolution in contrast to the TC-RFWM experiments. In particular, a large slit width (3 mm) that further reduced the frequency resolution was necessary to measure the low photon yield of the (0,2) band fluorescence. Nevertheless, the coarse determination of the vibrational origins for $v = 1$ and 2 of the high-spin $1^5\Pi_g$ state and $v = 3$ from the deperturbation study outlined in Section III A yields a solid base for comparison with the *ab initio* computations discussed in Sec. III D.

D. *Ab initio* computations

High level *ab initio* calculations have been performed for comparison with the experimentally determined rovibronic structure of the $1^5\Pi_u - 1^5\Pi_g$ band of dicarbon. The methodology of the computations has been reported recently⁴⁵ and is summarized briefly in the following. Potential energies were calculated at the multi-reference configuration interaction (MRCI) level of theory as implemented in the MOLPRO⁶¹ suite of programs. To establish the CI expansion, active orbital spaces and reference states were obtained in D_{2h} symmetry by applying complete active space self-consistent field (CASSCF)⁶² theory. The CASSCF states were generated in the full valence space ((8,8)-CAS) by state averaged calculations including the $1A_g$, $3B_{3u}$, $5B_{3u}$, $3B_{2u}$, $5B_{2u}$, $3B_{2g}$, $5B_{2g}$, $3B_{3g}$ and $5B_{3g}$ states at equal weights. D_{2h} symmetry labels correlate with $D_{\infty h}$ labels as follows: $A_g \rightarrow \Sigma_g^+$, $B_{2g} + B_{3g} \rightarrow \Pi_g$, $B_{2u} + B_{3u} \rightarrow \Pi_u$. The MRCI calculations were then carried out using the internally contracted MRCI method as explained in Refs. 63–66. These calculations were performed using the aug-cc-pCV6Z (ACV6Z) basis set and correlating all electrons (8 valence and 4 core electrons). In addition, the Davidson correction for quadruple excitation is included in the results.

In addition to the computations reported in Ref. 45, the method of explicitly correlated multi-reference configuration interaction,⁶⁷ implemented in the 2012 version of MOLPRO,⁶¹ MRCI-F12, has been applied. The calculations have been performed by utilizing the largest possible basis implemented in the 2012 version (cc-pCVQZ-F12, also named CVQZ-F12 here). Apart from the F12 method and the basis set, no modifications have been applied to the computations outlined above.

Rovibrational levels were computed by solving the one-dimensional radial Schrödinger equation on the *ab initio* potential energy curves (PEC) for a $3\Pi_u$, $1^5\Pi_u$, and $1^5\Pi_g$ by using the LEVEL software package from Le Roy.⁶⁰ Results from these calculations were verified by calculations using our own programs for the nuclear dynamics. For comparison of the two applied *ab initio* methods, MRCI and MRCI-F12, spectroscopic equilibrium constants have been evaluated by a non-linear least-squares fit to the expression

TABLE VIII. Computed spectroscopic constants for the $1^5\Pi_g$ and $1^5\Pi_u$ states and comparison with experimentally determined values by applying double-resonant four-wave mixing and LIF methods. T_0 is relative to the $a^3\Pi_u$, $v = 0$ state.⁴⁵ See text for the definition of $\omega_e x_e$, α_e , D_e , and β_e .

Parameter	$a^3\Pi_u$			$1^5\Pi_g$			$1^5\Pi_u$		
	ACV6Z	CVQZ-F12	Expt. ^a	ACV6Z	CVQZ-F12	Expt.	ACV6Z	CVQZ-F12	Expt.
T_0	0	0	0	29 225	29 308	29 258.592 2(48) ^b	50 932	51 010	51 049.799 5(48) ^c
r_e	1.312 3	1.311 9	1.311 946(16)	1.561 3	1.560 6	1.561 58(2) ^d	1.509 5	1.508 4	...
w_e	1 641.179(7)	1 642.33(2)	1 641.341(23)	994.118(11)	994.78(2)	991.201 9 ^e	907.7(1)	909.55(6)	...
$w_e x_e$	-11.318(3)	-11.248(7)	-11.658 0(58)	-9.743 4(41)	-9.836(6)	-9.852 0 ^e	-22.0(2)	-22.26(2)	...
$w_e y_e$	-0.041 4(4)	-0.054 7(10)	-0.000 83(41)	-0.008 5(6)	0.010 6(8)	0(fixed)	-6.60(5)	-6.6(fixed)	...
$w_e z_e$	0.001 81(2)	0.002 44(4)	0(fixed)	-0.001 21(3)	-0.002 15(4)	0(fixed)	0(fixed)	0(fixed)	...
B_e	1.631 404(28)	1.632 31(7)	1.632 35(4)	1.152 520(43)	1.153 38(6)	1.152 18 ^d	1.224(2)	1.226 4(6)	...
α_e	-0.016 442(6)	-0.016 45(2)	-0.016 57(3)	-0.015 428(10)	-0.015 44(1)	-0.016 10 ^d	-0.016(3)	-0.018(1)	...
$\gamma_e \times 10^3$	-0.027 50(43)	-0.028(1)	-0.027(5)	-0.087(1)	-0.085 0(9)	0(fixed)	-13.8(8)	-13.0(3)	...
$D_e \times 10^6$	-6.431(33)	-6.43(9)	-6.458 06(1) ^f	-6.116(50)	-6.12(7)	-6.227 3 ^f	-10.0(fixed)	-10.0(fixed)	...
$\beta_e \times 10^6$	-0.015(5)	-0.02(1)	...	-0.063(8)	-0.06(1)	...	0(fixed)	0(fixed)	...
$v_{\max}$	10	10	9	10	10	...	2	2	...
$J_{\max}$	29	29	...	29	29	...	10	10	...
$\tilde{\nu}_{\text{rms}}$	0.018	0.047	...	0.027	0.038	...	0.069	0.03	...
v_0	0	0	0	0	0	0	0	0	0
v_1	1618	1620	1 618.023 30(31)	975	975	969.1(2) ^d	842	844	823.435 5(47) ^d
v_2	3214	3216	3 212.722 62(41)	1930	1931	1913(1) ^d	1581	1583	...
v_3	4786	4790	4 784.111 3(31)	2865	2866	2 855.381 8(37) ^d	...	...	...
v_4	6335	6340	6 332.137 3(22)	3780	3782	...	...	...	...
v_5	7861	7867	7 856.824 2(17)	4676	4679	...	...	...	...
v_6	9363	9371	9 358.172 8(23)	5551	5555	5 533.427 8(887) ^e	...	...	...
B_0	1.623 22	1.624 13	1.624 045 1(22)	1.144 97	1.145 89	1.144 13(11) ^b	1.214 58	1.216 17	1.219 05(21) ^c
B_1	1.606 64	1.607 50	1.607 430 1(20)	1.129 17	1.130 00	...	1.170 76	1.172 25	1.165 88(46) ^d
B_2	1.590 14	1.591 06	1.590 761 5(27)	1.113 29	1.114 15	...	1.101 77	1.095 40	...
B_3	1.573 46	1.574 32	1.574 009(12)	1.097 31	1.098 20	1.095 84(37) ^d	...	...	...
B_4	1.556 78	1.557 63	1.557 175(14)	1.081 22	1.082 07	...	...	...	...
B_5	1.540 11	1.540 96	1.540 145(11)	1.064 99	1.065 80	...	...	...	...
B_6	1.523 39	1.524 25	1.523 437(14)	1.048 60	1.049 40	1.048 46(63) ^e	...	...	...

^aReference 36.
^bReference 41.
^cReference 45.
^dThis work.
^ePreliminary result (see text).
^fKratzer relation.⁶⁸

$$\begin{aligned}
 G(v) = & T_e + \omega_e(v + \frac{1}{2}) + \omega_e x_e(v + \frac{1}{2})^2 \\
 & + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 \\
 & + [B_e + \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2]J(J+1) \\
 & + [D_e + \beta_e(v + \frac{1}{2})]J^2(J+1)^2
 \end{aligned} \quad (2)$$

and taking into account the limitations of this expansion.⁴⁵ In the present paper as well as in Ref. 45, Eq. (2) corresponds to the version of the Dunham expansion that is used for polyatomic molecules.⁶⁹ Traditionally, the Dunham expansion for diatomic molecules is given with a minus sign in front of the $\omega_e x_e$, α_e , D_e , and β_e terms, which normally infers positive values for the anharmonicity rotational and centrifugal constants. The quality of the MRCI-F12 calculation is equal or superior to that with the aug-cc-pCV6Z basis but at significantly reduced computational costs of 1/2 to 2/3. The origins of the two quintet states relative to the $a^3\Pi_u$, $v = 0$ state agree with the experimental values to within roughly 50 cm^{-1} . An exception is the slightly increased deviation of the ACV6Z MRCI calculation of the $1^5\Pi_u$, $v = 0$ state of $\approx 120\text{ cm}^{-1}$. The agreement of the evaluated equilibrium constants listed in Table VIII reflects the close agreement of the potential energy curves (PECs) of the two methods. The accuracy of the applied methods is further demonstrated by comparing the calculated and experimental vibrational frequencies that are in relative good agreement but systematically higher than the experimental values. Disagreement is found for the first vibrational quanta of the $1^5\Pi_u$ state and can be rationalized by considering the extremely shallow and anharmonic PEC of this state.⁴⁵ As mentioned above, the experimentally determined vibrational frequencies for $v = 1$ and 2 of the $1^5\Pi_g$ by applying LIF (Section III C) are significantly less accurate than the constants obtained by deperturbation of the $d^3\Pi_g$, $v = 8$ (Section III A) and PFOODR of $1^5\Pi_u$, $v = 1$ (Section III B). Better agreement is obtained for the comparison of the computed and experimental rotational constants.

A comprehensive theoretical study of all levels of C_2 involved in the present spectroscopic investigations is in preparation and will be published separately.

IV. CONCLUSION

In this work, we report on the rovibrational characterization of the recently observed⁴⁵ high-spin electronic system ($1^5\Pi_u - 1^5\Pi_g$) of the dicarbon molecule. The quintet manifold is accessed by intersystem crossing through “gateway” states in strongly perturbed levels of the Swan band. Molecular parameters are determined for $v = 1-3$ and $v = 6$ for the $1^5\Pi_g$ state and for $v = 1$ of $1^5\Pi_u$ by applying non-linear four-wave mixing and LIF methods.

First, $v = 3$ of the lower quintet state is obtained by a deperturbation study of the $1^5\Pi_g$, $v = 3 \sim d^3\Pi_g$, $v = 8$ system by applying TC-RFWM. Unambiguous assignments by intermediate level labeling in the well-characterized and unperturbed (7,6) Swan system are performed. From these specific rovibronic levels, 44 transitions governed by strict dipole selection rules to the perturbed $d^3\Pi_g$, $v = 8$ level and 3 intercombination

transitions in the (3,6) $1^5\Pi_g - a^3\Pi_u$ band have been observed and yield molecular constants for $1^5\Pi_g$, $v = 3$. The results confirm the identity of the levels that govern the perturbation as suggested recently by Nakajima and Endo.⁵³

By taking into account accurately measured and well resolved transitions from the Fourier transform work of Tanabashi *et al.*,³⁶ the perturbation analysis could be significantly improved. These authors omitted perturbed transitions in their data reduction since these lines are often difficult to assign unambiguously in single-color spectra. However, many of these transitions are assignable on the basis of our initial deperturbation and are included in a global fit. Furthermore, data from Nakajima and Endo obtained by measuring LIF spectra in the (8,5) $d^3\Pi_g - c^3\Sigma_u^+$ band⁵⁹ have been combined in the final deperturbation process. In addition to the molecular constants of the $v = 3$ level in $1^5\Pi_g$, the values for T , λ , and σ for $d^3\Pi_g$, $v = 8$ are improved and the spin-orbit interaction constant is determined.

It is important to mention that this deperturbation study of $d^3\Pi_g$, $v = 8$ and the observations of the nominally forbidden transitions to $1^5\Pi_g$, $v = 3$ corroborate the energy gap between the triplet and quintet manifold that has been initially determined by analyzing the perturbed $d^3\Pi_g$, $v = 6 \sim 1^5\Pi_g$, $v = 0$ system.⁴¹

Based on the molecular constants obtained for $1^5\Pi_g$, $v = 0$ and $v = 3$, an extrapolation to $v = 6$ is feasible. The assessment predicts that this vibrational level is interacting with $d^3\Pi_g$, $v = 10$ near $J = 20$. An analysis of previously reported measurements³⁶ in the perturbed region of the (10,9) $d^3\Pi_g - a^3\Pi_u$ band reveals the presence of the quintet-triplet interaction and yields the preliminary molecular constants for ν_6 and B_6 . These values allow an estimation of the equilibrium constants ω_e and $\omega_e x_e$ of the $1^5\Pi_g$ state.

Second, by performing double resonant excitation *via* perturbed intermediate levels, the first excited vibrational level of the upper high-spin state ($1^5\Pi_u$, $v = 1$) is characterized with rotational resolution. 6 perturbed intermediate levels allow intersystem crossing from the thermally populated initial $a^3\Pi_u$, $v = 5$ state to 11 rotational levels of the $1^5\Pi_u$, $v = 1$ state. The measured transitions span the range of the rotational quanta $1 \leq J \leq 6$ and four spin-sublevels. Results yield accurate molecular constants and the excited vibrational energy $\Delta G_{1/2}$.

Third, the “gateway” for intersystem crossing is further utilized to excite $1^5\Pi_u$, $v = 0$ and perform dispersed fluorescence measurements. The progression to $v = 1$ and $v = 2$ of the lower quintet state $1^5\Pi_g$ is observed by spin-allowed emission in the quintet manifold.

The experimental findings are compared with high-level *ab initio* computations. The initial calculations at the MRCI level of theory using the large correlation consistent basis set aug-cc-pCV6Z⁴⁵ have been repeated with the method of explicitly correlated multi-reference configuration interaction applying the cc-pCVQZ-F12 basis set. The latter method yields results of an equal or slightly superior quality at significantly reduced computational costs. The near spectroscopic accuracy of the theoretical calculations facilitated significantly the experimental procedure to access the transitions in the quintet bands. Furthermore, the theoretical results

corroborate the experimentally determined identity of the observed vibrational levels.

ACKNOWLEDGMENTS

This work is supported by the Swiss National Science Foundation (Grant No. 200021_153170).

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