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Complementary cavity-enhanced spectrometers to investigate the OH + CH combination band in *trans*-formic acid

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We have used continuous-wave cavity ring-down and femto-Fourier transform-cavity-enhanced absorption spectrometers to record the spectrum of the OH-stretching + CH-stretching $(v_1 + v_2)$ combination band in *trans*-formic acid, with origin close to 6507 cm⁻¹. They, respectively, allowed resolving and simplifying the rotational structure of the band near its origin under jet-cooled conditions (T_{rot} = 10 K) and highlighting the overview of the band under room temperature conditions. The stronger B-type and weaker A-type subbands close to the band origin could be assigned, as well as the main B-type *Q* branches. The high-resolution analysis was hindered by numerous, severe perturbations. Rotational constants are reported with, however, limited physical meaning. The $v_1 + v_2$ transition moment is estimated from relative intensities to be 24° away from the principal *b*-axis of inertia. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4923256]

I. INTRODUCTION

Many investigations, including recent works by Ciurylo,¹ Di Natale,² Földes,³ Lehmann,⁴ Romanini,⁵ Ye,⁶ and their coworkers, demonstrate the ever increased impact of cavityenhanced laser spectrometers of various kinds in infrared molecular spectroscopy. In particular, continuous-wave cavity ring-down spectrometers (cw-CRDS),⁷ as developed by Romanini and co-workers using continuously tunable distributed feedback (DFB) lasers in the near infrared (NIR) spectral range,^{8,9} allowed reaching detection sensitivities as low as $\alpha_{min} = 6 \times 10^{-13} \text{ cm}^{-1}$.¹⁰ The absorption coefficient α is here defined as

$$\alpha = \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \frac{L}{cl},\tag{1}$$

where *c* is the speed of light, *L* and *l* are the lengths of the resonant cavity and of the absorption cell, respectively, τ and τ_0 are the ring-down times measured with and without sample, respectively, with

$$\tau_0 = -\frac{L}{c\ln R} \approx \frac{L}{c(1-R)},\tag{2}$$

where *R* is the cavity mirror (CM) reflectivity assumed to be identical for both mirrors. The equivalent absorption pathlength (l_{eq}) can be readily calculated from τ_0 , using the speed of light.

Cavity-enhanced absorption spectroscopic (CEAS) techniques with broad, frequency comb (femto) absorption sources are also being developed.¹¹ They similarly boost the sensitivity, down to, e.g., $\alpha_{min} = 1.3 \times 10^{-11}$ cm⁻¹ Hz^{-1/2} per spectral element,¹² with the absorption coefficient now defined as¹³

$$\alpha \approx -\frac{1}{l} \ln \left[1 - \frac{1 - R^2}{R^2} \left(\sqrt{\frac{I_0}{I}} - 1 \right) \right]$$
(3)

with, in addition to the symbols already defined, I_0 and I which are the intensities of the broad absorption source before and after absorption, respectively. In this case, using the cavity finesse (F) defined as

$$F = \frac{\pi R}{1 - R},\tag{4}$$

one can calculate

$$l_{eq} = F \times l/\pi \tag{5}$$

with l_{eq} dependent on the absorption coefficient. Some of these CEAS spectrometers are coupled to Fourier transform (FT) interferometers and benefit from (i) high, cavity-enhanced sensitivity exploiting coherent laser light and (ii) high-resolution, broad spectral coverage provided by FT instruments. This successful combination is illustrated in works recently achieved by Herman,¹⁴ Picque,¹⁵ and their co-workers.

As just referenced,^{3,14} two of these optical spectrometers were built at Université libre de Bruxelles, one based on cw-CRDS and another on femto-FT-CEAS. They altogether define the so-called FANTASIO+ setup,¹⁶ where FANTASIO stands for "Fourier trANsform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn" and the + for the different updates since the initial report in 2007.¹⁷

The quadrupole mass spectrometer in the setup, with a geometrically movable inlet, was used at the beginning of these instrumental developments to probe the performances of the supersonic expansion.^{17,18} It is not relevant to the present report.

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The cw-CRDS spectrometer in FANTASIO is coupled to a supersonic expansion. It allowed investigating van der Waals complexes at about 1 MHz instrumental resolution and, depending on the wavelength range, close to or above 1 km equivalent absorption pathlength through jet-cooled molecules. Rotational structures in intramolecular and sometimes intra + intermolecular vibrational bands were observed and analysed. Upper state predissociation lifetimes were measured from naturally broadened line shapes. The spectral ranges concerned-with only representative references listed-the 2CH excitation band in $C_2H_2^{19,20}$ 2NH in NH₃,²¹ 2OH in $H_2O_2^{3,22}$ and combination bands in HDO and $D_2O_2^{23,24}$ with these species bonded to various partners in the expansion including rare gases, in particular. Also, isolated, jet-cooled acetylene,²⁵ propyne,²⁶ and ammonia²⁷ were investigated.

The FT part in FANTASIO initially used a globar absorption source. It is today coupled to a femto/optical parametric oscillator (OPO) NIR broadband laser used as an absorption source for CEAS, defining the femto-FANTASIO spectrometer.^{28,29} We used this so-called femto-FT-CEAS technique to investigate O₂,²⁸ combination bands of acetylene isotopologues,³⁰ propyne,²⁶ ammonia,²⁷ CO₂ isotopologues,^{31,32} CS₂,³³ and OCS.¹⁴ These studies were carried on under room temperature conditions. The coupling of this technique to the supersonic expansion in FANTASIO was also demonstrated, thus probing jet-cooled isolated species using femtoFT-CEAS.¹³ The optical design in the two setups is schematized in Figure 1.

During each of the just referenced investigations on propyne²⁶ and ammonia,²⁷ both cw-CRDS and femto-FT-CEAS spectrometers from FANTASIO were used, however bringing information on different bands in each of the species. In this work, we aim at highlighting the complementarity of both spectrometers by merging their performances to investigate a single band. This band is the OH + CH, $v_1 + v_2$ combination band in *trans*-formic acid, with origin close to 6507 cm⁻¹.

Formic acid (HCOOH) is of both astrophysical³⁴ and atmospheric^{35,36} relevance. It exists in two planar structures, trans and cis, corresponding to the relative positions of the two hydrogen atoms with respect to the CO single bond.³⁷ Trans-HCOOH, that is about 800 times more abundant than cis-HCOOH at room temperature,^{38,39} is the rotamer relevant to the present investigation. The microwave and far infrared literature is reviewed in Ref. 40. Normal modes of vibration are characterized in Ref. 41 and mid and near infrared high-resolution spectroscopic investigations were reported.^{41–51} Work of more theoretical nature was also devoted to the vibrational energy pattern in this species.^{44,45,49,52–54} All of this literature demonstrate that vibrational bands of formic acid present very dense rotational structures almost systematically affected by strong and usually not fully modelled anharmonic resonances and/or Coriolis interactions. The $v_1 + v_2$



FIG. 1. Optical design in FANTASIO+ (more specific information on the experiments is provided in Section II). The cw-CRDS spectrometer (blue on-line) is based on a temperature-tuned, fibered DFB laser emitting in the NIR spectral range. One percentage of the light is used for reference measurements, half from a home-made Fabry-Perot (FP) etalon and half from a reference cell (RC) filled with an adequate absorber gas. The major fraction (99%) of the light is sent through an acousto-optic modulator (AOM) and mode-matched using two lenses (L) to the absorption cell. The sample is kept between the two high-reflectivity cavity mirrors (CM), one of which is positioned on a piezoelectric translator (PZT). A photodiode (PD) records the signal. The femto-FT-CEAS spectrometer (red on-line) includes a broadband femto/OPO NIR laser. The laser beam is phase matched using lenses (L) and sent using mirrors (M) into the absorption cell closed by high-reflectivity cavity mirrors (CM), one of which is positioned on a PZT. A RC can be inserted in the beam before the light is focused onto the entrance diaphragm of the high-resolution Fourier transform (FT) interferometer. The resulting interferences are sent onto a PD. The absorption cell is identical for both spectrometers, as in the figure whenever the supersonic expansion is used. It is not when room temperature femto-FT-CEAS data are recorded, using then a longer, dedicated cell for the latter experiments. Adequate electronics, not indicated on the scheme, is used to control most optical items and to record signals in both spectrometers.



FIG. 2. Recordings of $v_1 + v_2$ in *trans*-formic acid, with origin at 6507 cm⁻¹, using various experimental conditions; bottom: Bruker IFS120HR FT spectroscopy (p_{HCOOH} = 1 hPa, l = 48.16 m, FT-limited resolution = 0.03 cm⁻¹, 150 scans co-added, T ~ 300 K); middle: femto-FT-CEAS (p_{HCOOH} = 0.01 hPa, $l_{eq} \sim 10\,000$ m, FT-limited resolution = 0.02 cm⁻¹, 400 scans co-added, T ~ 300 K); top: jet-cooled cw-CRDS (Ar flowing (1.5 sccm) in liquid HCOOH, p_{out} = 590 hPa, p_{in} = 0.01 hPa, $l_{eq} \sim 750$ m, molecular FWHM-limited resolution ~ 0.003 cm⁻¹, T_{rot} ~ 15 K). The various bands are identified in the bottom spectrum.

(OH + CH) band of interest to the present work was previously reported from low-resolution FT data, only.⁴¹ This previous work mentions that $v_1 + v_2$ is about 20 and 3 times weaker than the surrounding $2v_1$ and $2v_2$ bands, respectively, making it one of the weakest bands identified in the spectrum from bottom up to 13500 cm⁻¹.⁴¹ Figure 2 compares a conventional FT recording from this earlier study (bottom: p_{HCOOH} = 1 hPa, l = 48.16 m, FT-limited resolution = 0.03 cm⁻¹) to the data presently recorded using room temperature femto-FT-CEAS (middle: $p_{\text{HCOOH}} = 0.5$ hPa, $l_{eq} \sim 10000$ m, FTlimited resolution = 0.02 cm^{-1}) and jet-cooled cw-CRDS (top: $p_{\text{HCOOH}} \sim 0.001$ hPa, $l_{eq} \sim 750$ m, molecular FWHM-limited resolution $\sim 0.003 \text{ cm}^{-1}$). The bottom, conventional FT spectrum in this figure was recorded earlier and corresponds to a sample pressure low enough to avoid saturating the 2OH absorption band. Higher-pressure spectra were used at the time to spot the OH + CH band.⁴¹ The conventional FT spectrum does cover a much broader range than presented. The spectral coverage in the femto-FT-CEAS spectrum is about 100 cm^{-1} , as determined by the OPO optical settings. It decreases to about 30 cm⁻¹ in the cw-CRDS spectrum, corresponding to the tunability of a single DFB laser diode. Spectral coverage could be increased for both laser techniques by modifying the OPO settings or by using another DFB diode. Another typical trend when comparing these techniques is the obvious increase in S/N for the OH + CH band from bottom to top spectra in Figure 2 (from ~ 1 to 10 to 25). It goes along with the increase in the $p \times l$ factor when using FT recording in the bottom and middle spectra. This factor evolves from 50 to 5000 hPa \times m, respectively. It is further boosted by much

lower noise in the DFB-diode laser spectrum (top, with $p \times l = 0.75$ hPa \times m, only). The (top) jet-cooled cw-CRDS spectrum also demonstrates obvious gain in resolution, limited by the FT-based instrumentation in the other spectra. It furthermore shows significant increase in spectral simplification, because of the low rotational temperature (T_{rot} ~ 10 K) resulting from the use of a supersonic expansion.

Information on the experimental setup is detailed in Section II. The rotational analysis of the OH + CH band, that will exploit data from the two cavity-enhanced spectra presented in Figure 2, is presented and discussed in Section III, before concluding.

II. EXPERIMENTS

Critical features of the two experimental setups are recalled here, from more complete presentation already published in the literature (see Refs. 14 and 19 in particular). Most symbols in italic hereafter refer to those used in Figure 1. Formic acid was from Merck (HCOOH 98%-100%).

A. Femto-FT-CEAS in FANTASIO

A femto/OPO laser beam (*Femto/OPO laser*, Coherent Chameleon ULTRA II/PP810) with about 100 cm⁻¹ wide tunable spectral output is injected into a high-finesse cavity using two lenses (L, f = 50 mm each). We used a set of mirrors (*CM*, Layertec) with a reflectivity varying between 99.98% and 99.993% in the range from 6100 to 6700 cm⁻¹. They

correspond to F = 6100-49000 and $l_{eq} = 1500-12000$ m, respectively. One of them is mounted on a piezoelectric translator (PZT, HPST 1000 modulator) modulating the length of the cavity, a newly arranged static cell about 145 cm long, at 20 kHz. In this way, cavity modes are scanned and on the average, every laser mode is equally transmitted, leading to a smooth transmission spectrum. A HoYag type optical Faraday isolator (OI, Thorlabs) is placed between the laser source and the cavity to avoid optical feedback into the laser cavity. The laser beam going out of the cavity is directly injected into a high-resolution continuous scan FT spectrometer (Bruker IFS120HR) equipped with an InGaAs photodiode (PD). In the present experiments, the laser beam diameter was focused to 10 μ m on the entrance FT iris, set at 1.15 mm in diameter. The FT resolution was set to 2×10^{-2} cm⁻¹ (defined as $0.9 \times$ maximum optical path difference). Four hundred scans were co-added. As stated in Ref. 14, these conditions correspond to a minimal absorption coefficient of 3×10^{-9} cm⁻¹. Since the resolution is 0.02 cm⁻¹ and the bandwidth 100 cm⁻¹, thus defining 5000 spectral elements, it corresponds to an absorption sensitivity of 6×10^{-13} cm⁻¹ per spectral element. Accounting for the 1.5 h acquisition time, it also corresponds to a rms equivalent absorption coefficient of 4.41×10^{-11} cm⁻¹ Hz^{-1/2}, using current literature units.^{12,55} The pressure of formic acid was 0.5 hPa. The sample contained traces of water, whose absorption line wavenumbers, from Ref. 56, were used to calibrate the data using the WSpectra software.⁵⁷ Thus, the reference cell (RC) indicated on Figure 1 was not used in the present case. The calibration procedure is expected to result in $\pm 2 \times 10^{-2}$ cm⁻¹ and $\pm 1.8 \times 10^{-3}$ cm⁻¹ accuracy and precision, respectively.

We actually also recorded femto-FT-CEAS data in a multi-nozzle,¹³ jet-cooled expansion of formic acid, using the same pumping setup as described in Sec. II B. The S/N was, however very limited, requiring significantly increasing the relative amount of HCOOH vs. Ar in the expansion, hence reducing the cooling effect. In the end, these data did not bring enough relevant information and were discarded.

B. cw-CRDS in FANTASIO

A tunable laser diode emitting in the 1.54 μ m range (DFB *laser*, ILX Lightwave, 1 MHz linewidth) is injected through an acousto-optical modulator (AOM, AA Opto-Electronic MGAS 80-A1) into a high-finesse cavity using two lenses (L, f = 30 and 50 mm). A single DFB diode was used, scanning around the band centre. We use a set of two mirrors (CM, Layertec) with a reflectivity of about 99.9985% each, and separated by some 54 cm. One of them is set onto a PZT (HPST 1000/15-8/5). The operating procedure is very similar to that developed by Romanini and co-workers and not repeated here.^{8,9} To increase the ring-down event rate, a home-made tracking circuit is used.⁵⁸ Typically, about 200 ringdowns per spectral point are fitted. The sensitivity of the setup is measured to be up to 5×10^{-10} cm⁻¹. Line positions are calibrated using the procedure described in Ref. 19, passing a small fraction (0.5%)of the fibered laser beam into a home made, temperaturestabilized Fabry-Pérot (*FP*) etalon and another fraction (0.5%)into a RC containing acetylene, with reference wavenumbers

taken from Ref. 59. The signal from the *PDs* is used to produce calibrated spectral data, from a LabVIEW calibration routine developed by Cermàk.⁶⁰ The procedure results in better than $\pm 1 \times 10^{-3}$ cm⁻¹ accuracy and precision.

The supersonic expansion is produced using two turbomolecular pumps (Leybold MAG W3200 CT, 2850 l/s) backed by a primary pump (Alcatel ADS 860 HII group). We used here a slit nozzle about 1 cm long and 30 μ m wide. Some 4250 sccm Ar (Air Liquide), where sccm denotes cubic centimeter per minute at standard conditions for temperature and pressure, was bubbled through liquid formic acid and the mixture was injected into the expansion. The reservoir (p₀) and the residual (p_∞) pressures were 590 and 0.01 hPa, respectively. The spectral simulation demonstrated that T_{rot} ~ 10 K.

III. VIBRATION-ROTATION ANALYSIS

We initially considered both series of data, from femto-FT-CEAS and cw-CRDS spectra. The analysis faced a large number of perturbations of various strengths. We attempted unraveling them in many ways, building on our previous expertise on formic acid^{45,48,49} and exploiting theoretical information from the literature on the vibrational energy pattern.^{52,54} Unfortunately, neither perturbation mechanism could be reliably extracted from the rotational analysis nor precisely predicted from the literature to help in the analysis. In the end, we limited the rotational analysis to line assignments, extracting minimal sets of constants from those lines less perturbed. We first focused on the jet-cooled (cw-CRDS) spectrum. We then used the related results to try interpreting the room temperature (femto-FT-CEAS) data, not accounting for hot bands. The presentation of the results hereafter follows the same strategy, thus not reporting on unsuccessful attempts to deperturb the spectrum. All assigned lines are listed in the supplementary material.⁶¹

A. Jet-cooled data

The $v_1 + v_2$ hybrid band, with dominant B-type and weaker A-type characters, was readily identified from the cw-CRDS data. The analysis was initiated by following series of lines which, according to the assumed intensity pattern at ~10 K temperature, were expected to be strong enough to be observable. These assignments were confirmed by checking the ground state combination differences for A- and B-type transitions. The hybrid character of the $v_1 + v_2$ band was useful to confirm the assignments. Indeed, the analysis proved to be very difficult because of strong perturbations. Several groups of perturbed lines presenting identical shifts and expected intensities, as compared to the prediction, could be identified. Each of these groups clearly involved the same upper state and the individual lines could then be reliably assigned, despite not being satisfactorily fitted.

In the fitting procedure, we used and constrained the ground state parameters from Ref. 40. The main parameters are listed in the first column of Table I. Many more ground state distortion constants are produced in Ref. 40, which were also used and constrained but that are not listed in Table I for the sake of concision. The lower state energy levels were

TABLE I. Vibrational energy, selected rotational constants, and standard deviation of the fit, σ (all in cm⁻¹), of *trans*-formic acid for the ground and $1^{1}2^{1}$ vibrational states (see text for details).

	Ground ^a	CRDS data ^b	CRDS + CEAS data ^b
Ev	0	6507.0592(31)	6507.0709(150)
А	2.585 529 555 5	2.578 96(190)	2.570 86(170)
В	0.402 115 009 71	0.387 551(160)	0.387 977(840)
С	0.347 444 162 94	0.354979(140)	0.353 528(840)
$\Delta_{\rm K}$	$5.6781541 imes 10^{-05}$	ş	$2.653(440) \times 10^{-04}$
Δ_{JK}	$-2.87602718 imes 10^{-06}$	ş	$-5.04(170) \times 10^{-05}$
Δ_J	$3.33366785 imes 10^{-07}$	ş	$-6.66(130) \times 10^{-06}$
$\delta_{\rm K}$	$1.4268630 imes 10^{-06}$	ş	$4.50(110) \times 10^{-04}$
σ		0.001 50	0.019

^aConstrained from Predoi-Cross et al., Ref. 40.

^bQuoted uncertainties are one standard deviation in the units of the last quoted digit. Constants quoted with a § were maintained fixed to their ground state values, from Predoi-Cross *et al.*, Ref. 40. All other distortion constants produced in Ref. 40 were included in the fitting procedure and constrained to their ground state value in both lower and upper states.

calculated and added to the observed line positions of $v_1 + v_2$ to get a list of experimental $1^{1}2^{1}$ upper state energy levels. These upper state level energies were inserted in a least squares fit to get the band center and rotational constants for the $1^{1}2^{1}$ excited state. Unfortunately, because of numerous resonances, less than half of the observed $1^{1}2^{1}$ energy levels (16 over 41) could be considered in this calculation. As a consequence, only A, B, and C rotational constants were refined during this calculation, using an A-reduced Watson type Hamiltonian written in Ir representation.⁶² These parameters are quoted together with their estimated uncertainties in the second column of Table I. All other distortion constants were constrained to their ground state value. A significant fraction of the observed lines could not be assigned. It is estimated to be 30% of all lines in the cold spectrum. It likely arises from dark transitions and from higher J/K levels that could not be accounted for. The overall agreement between observed and simulated spectra, with relative intensity parameters in the simulation detailed

and discussed in Section III C, is presented in Figure 3. In the bottom spectrum, the calculated positions of the perturbed lines that could be assigned were replaced by their observed positions.

B. Room temperature data

Using the parameters obtained during the investigation of the cw-CRDS spectrum, it was possible to identify some additional lines on the room temperature, femto-FT-CEAS spectrum of $v_1 + v_2$, and therefore to increase the number of experimental energy levels for the $1^{1}2^{1}$ excited state. These new energy levels were inserted in a new least squares fit calculation together with those obtained during the investigation of the jet-cooled data. We also systematically assigned the Btype K-subbands beyond those appearing on the jet-cooled spectrum. From simulations (see Sec. III C), we identified the J-values of the lines with the maximum strength expected to define the related Q branches on the spectrum. About a hundred lines were included in the fitting procedure as well for each ${}^{R/P}Q$ branch from $K_a = 2$ to 9. In this way, it was possible to determine another set of band center and A, B, and C rotational constants together with some centrifugal distortion constants for the 1121 excited state. As during the first calculation (see Section III A), all other distortion constants from Ref. 40 were used and constrained to their ground state value for both lower and upper vibrational states. Again, only a fraction of the $1^{1}2^{1}$ assigned energy levels could be fitted (42) out of 81). The rotational parameters are quoted together with their estimated uncertainties in the third column of Table I. It is clear from columns 2 and 3 in Table I that the two procedures lead to similar values of A, B, and C rotational constants. As will be discussed in Sec. III C, these parameters are effective ones with poor physical meaning. The calculated band shape in the spectral range including those fitted Q heads is presented in Figure 4. The simulation has been adapted, as in Figure 3 to include the few "calculated and replaced" line positions. The overall agreement looks reasonable, however, not precisely accounting for most of the individual line positions.



FIG. 3. cw-CRDS spectrum of $v_1 + v_2$ in *trans*-formic acid recorded under jet-cooled conditions (see text for more experimental details). Top (black on-line): observed spectrum; middle (red on-line): calculated spectrum after replacing perturbed positions by observed ones (see text for more details); bottom (blue on-line): calculated spectrum. The calculated spectra correspond to $T_{rot} = 10$ K and $|^A\mu_{12}|/|^B\mu_{12}| = 0.45$.



FIG. 4. Major portion of the femto-FT-CEAS spectrum of $v_1 + v_2$ in *trans*-formic acid recorded at room temperature (see text for more experimental details), observed (top, black on-line), and simulated (bottom, red on-line) (see text for more details).

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C. Discussion

According to ab initio predictions (see Table VII in Ref. 52), the 2^1 and 1^1 states are affected by anharmonic resonances such as $2^1 \Leftrightarrow 3^1 4^1$, $2^1 \Leftrightarrow 3^1 5^1$ and $1^1 \Leftrightarrow 2^1 7^1$, $1^1 \Leftrightarrow 3^2$. In addition, it is very likely that both fundamental states are affected by local Coriolis resonances, as confirmed by the partial rotational analyses in the literature.^{49,51} Such vibrationrotation resonances were furthermore reported from the rotationally resolved investigation of v_1 and v_2 of *trans*-formic acid embedded in liquid helium droplets.⁵⁰ Therefore, considering that the 1^1 and 2^1 states are significantly perturbed, it is presumed that the scheme of resonances affecting the $1^{1}2^{1}$ vibrational energy level is really complex. The very high value of the inertial defect $\Delta_{12} = -2.55 \ \mu \text{\AA}^2$ associated to the principal rotational constants (as calculated from columns 1 and 2 in Table I) confirms this statement. It is further supported by the unsatisfactory comparison, not further detailed here, between the experimental vibration-rotation constants, α , obtained from the values listed in Table I and those predicted from *ab initio* calculations.⁵² These various unidentified vibration-rotation resonances thus strongly reduce the physical meaning of the principal rotational constants listed for $1^{1}2^{1}$ in Table I, as previously mentioned. As an another evidence for strong perturbation mechanisms, an intensity raise is observed around 6565 cm⁻¹ in the observed spectrum, not shown here, that demonstrates the presence of an additional, unidentified band with origin likely to be just beyond the high wavenumber end of the recorded range (6580 cm^{-1}).

To further evidence the resonances, a detailed comparison is performed on the cold spectrum in Figure 5. Two simulations are presented. The bottom spectrum (blue on-line) corresponds to that calculated using the constants listed in columns 1 and 2 of Table I. In the top spectrum (red on-line), we replaced the calculated positions of the perturbed lines that could be assigned (see Sec. III A) by their observed positions. A- and B-type lines are indicated using geometrical forms and ar-



FIG. 5. Small portion of the cw-CRDS spectrum of $v_1 + v_2$ in *trans*-formic acid recorded under jet-cooled conditions (see text for more experimental details). Bottom (blue on-line): calculated spectrum; middle (black on-line): observed spectrum; top (red on-line): calculated spectrum after replacing perturbed positions by observed ones (see text for more details). The calculated spectra correspond to $T_{rot} = 10$ K and $|^A\mu_{12}|/|^B\mu_{12}| = 0.45$.

rows, respectively. Perturbations, unfortunately unassigned, are obvious from the comparison with the observed spectrum (middle part, black on-line).

As mentioned before, we used $T_{rot} = 10$ K in Figures 3 and 5 to optimally reproduce relative line intensities. We also determined from relative intensities the ratio between A- and B-type components of the $v_1 + v_2$ transition moment operator,

$$|^{A}\mu_{12}|/|^{B}\mu_{12}| \approx 0.05 \text{ Debye}/0.11 \text{ Debye}$$
 (6)

which was used in the simulation. This ratio actually corresponds to a transition moment operator μ_{12} oriented about 24° away from the *b*-axis. No definite information can be derived on its more precise orientation from the present data.

IV. CONCLUSION

We have used the cw-CRDS and femto-FT-CEAS spectrometers in FANTASIO+ to record the spectrum of the OH + CH $(v_1 + v_2)$ combination band in *trans*-formic acid, with origin close to 6507 cm⁻¹. The latter spectrometer provided an overview of the band under room temperature conditions, mainly revealing B-type K-subbands and a very limited number of regularly spaced and assignable R/P series of lines. The former spectrometer allowed the jet-cooled spectrum of the band (T_{rot} \sim 10 \text{ K}) to be recorded and analysed, revealing stronger B-type and weaker A-type subbands with assignable structures close to the band origin. The high-resolution analysis was hindered by numerous severe perturbations that could not be accounted for despite much effort. Nevertheless, upper state rotational constants could be obtained from the fit of 54 lines in the cold spectrum. Additionally, 94 room temperature lines could be assigned. A complementary set of upper state constants was produced by accounting for the main structures in the room temperature spectrum in addition to the assigned lines in the cold spectrum. The a and b dipole transition moments were estimated from the cold data to be 0.05 and 0.11 D, respectively, corresponding to a transition moment directed some 24° away from the principal *b*-axis of inertia. Finally, the emphasis is to be set again on the complementarity of the data specific to the two spectrometers in the FAN-TASIO setup. One spectrometer (femto-FT-CEAS) ensured broadband recording under room temperature conditions. The other (cw-CRDS coupled to a supersonic expansion) provided increased resolution, sensitivity, and spectral simplification, revealing the rotational structure around the band origin. The merge of both sets of data provided a complementary way to address the high-resolution analysis of a weak and dense vibration-rotation band. It is both unfortunate and challenging that the rotational structure demonstrates an extended pattern of interaction problematic to unravel, despite it is a band with only two quanta of excitation in a limited-size molecule not presenting complex low amplitude movement, and furthermore characterized by sound theoretical information in the literature.

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