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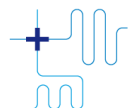
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Rovibrational spectroscopy of 1,4-dioxane in the mid-infrared range from high resolution jet-cooled and long path cell measurements

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Pierre Asselin,^{1,a)} Jordan A. Claus,^{2,b)} Colwyn Bracquart,^{2,3,c)} Manuel Goubet,² Olivier Pirali,⁴ Robert Georges,⁵ and Arnaud Cuisset³

AFFILIATIONS

¹ Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, Paris F-75005, France

² Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France

³ Université du Littoral Côte d'Opale, UR4493, LPCA, Laboratoire de Physico-Chimie de l'Atmosphère, F-59140 Dunkerque, France

⁴ Université de Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, F-91405 Orsay, France

⁵ Université de Rennes, CNRS, IPR (Institut de Physique de Rennes)—UMR 6251, F-35000 Rennes, France

^{a)} Author to whom correspondence should be addressed: pierre.asselin@sorbonne-universite.fr

^{b)} Present address: Institute of Condensed Matter and Nanosciences, Université catholique de Louvain (UCLouvain), Louvain-la-Neuve, Belgium.

^{c)} Present address: Laboratoire de Physique des Lasers, CNRS, Université Sorbonne Paris Nord, Villetaneuse, France.

ABSTRACT

This study presents a high-resolution rovibrational investigation of 1,4-dioxane in the mid-infrared region, motivated by the need for accurate spectroscopic data in the context of atmospheric monitoring of this emerging pollutant. Jet-cooled spectra were recorded using two complementary setups: a continuous supersonic jet coupled to the Fourier transform spectrometer of the AILES beamline at the SOLEIL synchrotron facility (Jet-AILES) and a quantum cascade laser spectrometer coupled to a pulsed jet (SPIRALES). These measurements were combined with long-path cell spectra at room temperature and supported by anharmonic quantum chemical calculations. Four fundamental vibrational bands (ν_{34} , ν_{33} , ν_{16} , and ν_{15}) were analyzed at high resolution, leading to the assignment of more than 6100 rovibrational transitions. A global fit yielded accurate ground- and excited-state rotational and centrifugal distortion parameters. The results significantly improve the spectroscopic characterization of 1,4-dioxane and provide reliable line lists for future atmospheric detection in the mid-infrared range.

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I. INTRODUCTION

1,4-Dioxane (DX) belongs to the family of cyclic ethers emitted in the atmosphere by various anthropogenic sources. In particular, DX is used as an industrial solvent for cellulose acetate, resins, oils, and waxes. A recent study reveals a dramatic increase in global industrial discharges with an emission profile now dominated by the production of plastics and surfactants. The study identifies these industrial stacks as significant point sources of atmospheric loading that were previously under-reported in global inventories. This

highlights the need for more accurate emission inventories and coordinated international regulatory efforts to address the growing environmental threat posed by DX.¹

The atmospheric fate of DX is dominated by its reaction with the OH radical; its main reaction product (90%) is ethylene glycol diformate.² DX is a moderately persistent volatile organic compound (VOC) with an atmospheric lifetime of 1–3 days but reactive enough to influence air quality hundreds of kilometers downwind off from the emission source.³ Direct gas-phase secondary organic aerosol (SOA) yields are limited by the fragmentation of these

intermediates. Nevertheless, the formation of highly water-soluble dicarbonyls suggests a significant contribution to the aqueous-phase SOA budget in humid or cloud-impacted environments.⁴

While DX is tightly regulated in water, its monitoring in ambient air has historically been less frequent, often tied to industrial emission assessments or vapor intrusion from contaminated groundwater. Lin *et al.* in Ref. 5 underline the potential for shallow plumes to produce high levels of DX vapor and the need to quantify concentrations, exposures, and health risks of this compound. To this end, they developed a sensitive and rapid analytical method for airborne DX that is applicable in high-humidity environments. The method achieves a very low limit of detection (~ 20 pptv) using passive sampling, automated thermal desorption, and gas chromatography/mass spectrometry. To our knowledge, there is no demonstration of non-intrusive path monitoring of DX at trace level.

Besides many studies on the kinetics and mechanisms of dioxane atmospheric reactivity, very few gas-phase spectroscopic studies of these cyclic ethers have been reported. The pioneering gas-phase infrared (IR) study of DX by Ramsay⁶ in 1947 enabled to observe 9 vibrational mode frequencies in the 700–1500 cm^{-1} range. The five possible ring structures for DX, namely “planar” (D_{2h}), “chair” (C_{2h}), “symmetrical boat” (C_{2v}), “twisted boat” (C_2), and an irregular configuration with no symmetry, were distinguished by the different numbers of fundamentals observed in the IR and Raman spectra, which favored the “chair” conformation as the most stable, in agreement with an earlier electron-diffraction study. Much later, a 2 cm^{-1} resolution gas-phase spectrum covering the whole IR range was recorded at NIST,⁷ and Ellestad and Klaboe⁸ published a comprehensive study combining IR spectra of DX and its fully deuterated isotopologue with Raman spectra assigned in both liquid and gas phases over the 80–4000 cm^{-1} range. From a normal coordinate analysis to derive the force field and the root-mean-square amplitudes of vibration, they concluded that the molecule has C_{2h} symmetry in its ground-state (GS). In the “chair” conformation DX has no permanent dipole moment, consequently, high-resolution IR spectroscopy offers the best route to derive accurate GS molecular parameters. In 1993, Brown *et al.*⁹ reported the rotationally resolved spectrum of the ν_{15} band of DX using a supersonic jet coupled with diode lasers, providing the first accurate sets of GS and $\nu_{15} = 1$ vibrational excited state (ES) molecular parameters. Owing to the environmental contamination proven of DX, its quantification and trace-level detection are important for atmospheric pollution studies and require accurate laboratory measurements. To this end, Chandran and Varma¹⁰ used a sensitive Fourier Transform (FT) incoherent broadband cavity-enhanced spectrometer operating in the near-IR to identify DX spectral signatures without interference from water for *in situ* spectroscopic detection. Finally, Den *et al.*¹¹ measured femtosecond Raman rotational coherence spectroscopy (RCS) transients of DX in a gas cell at 293 K and in a supersonic jet at 130 K, fitting them to an asymmetric-top model to obtain GS rotational constants. In this work, they have combined vibrationally averaged rotational constants calculated with a highly correlated coupled-cluster method and cc-pCVXZ basis-set series with extrapolation to the ground state experimental constants allowing a very accurate determination of DX’s equilibrium ground state structure.

The present study aims to determine the rovibrational parameters of most intense DX bands in the mid-IR range. Taking advantage of the broadband spectral coverage of the high-resolution FT spectrometer coupled to a continuous supersonic jet on the IR beamline of the SOLEIL synchrotron (Jet-AILES setup) and the sensitivity of a quantum cascade laser infrared spectrometer coupled to a pulsed supersonic jet (SPIRALES setup at MONARIS), we performed jet-cooled measurements at low rovibrational temperatures. This drastically tightened the rotational population distribution of fundamental cold bands and reduced the rovibrational line density from hot band sequences originating in the 5 lowest vibrational modes of DX below 500 cm^{-1} . Our experimental strategy, based on global fits of very accurate and sensitive low-temperature rovibrational measurements and successfully demonstrated previously for furfural,¹² was applied to DX to improve the precision of molecular parameters for the GS and the $\nu_{15} = 1$ ES, to determine a new parameter set for three previously unstudied ES ($\nu_{34} = 1$, $\nu_{33} = 1$, and $\nu_{16} = 1$) and to provide extensive rovibrational line lists for future mid-IR detection in the maximal transparency atmospheric window from 8 to 14 μm .

II. METHODS

A. Fourier transform infrared experiments

1. Jet-AILES

The Jet-AILES setup has been described in detail in previous works.¹³ The continuous supersonic expansion is generated by a heatable 60 mm long slit nozzle with 60 μm width in a vacuum chamber evacuated by one primary rotary pump and two secondary roots pumps delivering a pumping speed of 1850 $\text{m}^3 \text{h}^{-1}$. Total gas flow rates up to 40 standard liter per minute (slm) can be achieved with a maximal residual pressure of about 1 hPa.

In the present study, the stagnation pressure was limited to 370 hPa to prevent argon clustering. The high-pressure reservoir and the low-pressure vacuum chamber were equipped with Baratron pressure gauges. The injected gases were regulated with a series of mass-flow controllers (Bronkhorst). The liquid DX (99.8%, Sigma-Aldrich) sample was evaporated in a controlled manner using a Controlled Evaporation Mixer (CEM, Bronkhorst) supplied with regulated flows of argon as buffer gas and liquid DX. The slit nozzle, the gas supply line, and the CEM were maintained at 400 K to avoid any recondensation of the sample downstream of the CEM and to prevent the nozzle temperature from dropping down due to supersonic jet cooling. The vacuum chamber is connected to the high-resolution Bruker IFS 125 FTIR spectrometer installed on the AILES beamline of the SOLEIL synchrotron facility. The present jet experiments relied on the spectrometer’s internal mid-IR source (Globar). After being modulated, the IR light beam was focused at about 2 mm from the exit of the planar supersonic expansion and collected by a liquid-nitrogen-cooled HgCdTe detector. The vacuum chamber was isolated from the spectrometer and the detectors compartment with two ICS windows placed on either side of the supersonic expansion. A KBr beam splitter was used to record spectra in the 600–1800 cm^{-1} spectral range. A series of 200 low-resolution (0.1 cm^{-1}) reference scans were systematically

averaged before injection of DX in order to calculate the transmittance spectra.

Supersonic expansion parameters of Jet-AILES were adjusted to 1.5 slm of DX diluted in 10 slm of argon with a stagnation pressure in the 320–370 hPa range to optimize the signal-to-noise ratio (SNR) of vibrational signatures. Argon was chosen instead of helium because it lowers more efficiently the rotational temperature, thereby increasing the intensity of rovibrational lines with low J angular quantum number. A low-resolution spectrum was first recorded to locate the main absorption features of DX between 700 and 1500 cm^{-1} . The jet-cooled spectrum in the fingerprint mid-IR region was obtained by Fourier transforming 100 co-added interferograms at 0.5 cm^{-1} resolution. High-resolution spectra were then recorded at the maximum resolution of the spectrometer (0.001 02 cm^{-1}). To achieve the best SNR in the 850–1300 cm^{-1} region (where the most intense vibrational bands of DX lie), two available band-pass filters were successively installed, covering the 840–1180 and 670–1300 cm^{-1} ranges. By limiting the number of photons reaching the detector, the narrower filter was preferentially used to record the ν_{34} and ν_{16} bands around 880 and 1140 cm^{-1} , thus minimizing the number of co-added scans required. The broader filter was used to record the ν_{15} band around 1260 cm^{-1} . A total of 66 scans for the 840–1180 cm^{-1} range and 90 scans for the 670–1300 cm^{-1} range were accumulated at the maximal resolution of 0.001 02 cm^{-1} . The absolute wavenumber scale for the Bruker IFS 125 HR spectrometer was evaluated in the mid-IR range by comparing the frequencies of few tens of rovibrational lines recorded in the ν_2 O–C–O bending region with those reported in the last update of HITRAN database, enabling to determine a line frequency average correction equal to 0.000 05 cm^{-1} with a standard deviation equal to 0.000 2 cm^{-1} . Besides that, taking into account both signal-to-noise ratio and spectral congestion of Jet-AILES rovibrational measurements at maximal resolution (0.001 02 cm^{-1}), their line position accuracies are estimated to be 0.000 5 cm^{-1} .

2. Long path cell

Room temperature measurements in the mid-IR range were performed alongside the Jet-AILES experiments to refine quartic centrifugal distortion parameters of the ground and excited states using a White-type multipass cell coupled to the high-resolution Bruker IFS 125 FTIR spectrometer, with an absorption path length of 100 m. The multipass cell was equipped with Au–Cr coated glass mirrors and isolated from the FT spectrometer by ZnSe antireflection coated windows. High resolution measurements were made with the same beam splitter, IR source, and detector as for Jet-AILES ones. An acquisition time of 18 h, corresponding to the co-addition of 372 scans at the maximum resolution of 0.001 02 cm^{-1} , was required to obtain sufficient SNR for the three most intense DX bands in the mid-IR range. Using the same arguments mentioned in Sec. II A 1, line-position accuracy was estimated to 0.000 2 cm^{-1} for the rovibrational lines of these bands.

B. Mid-infrared laser experiments

IR direct absorption experiments were also performed with the SPIRALES setup, a jet-cooled laser spectrometer that couples an external-cavity quantum cascade laser (EC-QCL) to a pulsed supersonic free jet. SPIRALES has been described in detail elsewhere.^{14,15}

The IR source is a continuous-wave room-temperature mode-hop-free EC-QCL (Daylight Solutions) of 10 MHz spectral width. The QCL chip and a diffraction grating are mounted on a piezoelectric transducer to form an external cavity; high-resolution measurements are obtained by scanning the cavity length. DX jet-cooled experiments used an EC-QCL covering the 1015–1065 cm^{-1} range (Model 41095-MHF). About 8% of the total power is sent to an etalon of 0.025 cm^{-1} to provide a relative frequency scale. Absolute frequency calibration is obtained by passing about 8% of the IR power through a 10 cm cell containing a known reference gas (methanol in the present range). A linear interpolation of the etalon peak positions establishes the relationship between the voltage applied to the piezoelectric transducer and the relative frequency. This frequency scale allows correction of the free spectral range value fixed at the beginning of each experiment; a typical frequency accuracy of about 0.000 5 cm^{-1} is achieved by comparing measured line positions with frequency standards from the HITRAN2020 database.¹⁶ About 85% of the initial laser power is directed to a multipass absorption cavity, based on an astigmatic variant of the off-axis resonator Herriott configuration, installed in the supersonic expansion chamber, perpendicularly to the jet axis.

Pulsed planar expansions synchronized with the laser wavelength sweep, together with the simple implementation of multipass optical cavities make it possible to work at high backing pressures with very diluted samples. The molecular jet was produced from a pulsed 0.9 mm-diameter pin hole nozzle (General Valve Series 9). The seeded mixture DX/Ar was cooled by converting the circular flow of the standard valve configuration into a planar expansion using six-way distribution gas channel capped with two modified industrial blades, forming a 40 mm-long, 100 μm -wide slit aperture. The liquid DX sample was swept at room temperature at about 20 hPa by the Ar flow. Under these planar expansion conditions, residual Doppler broadening, due to non-orthogonal crossings between the speed vector of the jet-cooled molecules and the several infrared paths of the astigmatic optical cavity, occurring at different axial positions of the planar expansion, is minimized and experimental full-width at half maximum linewidths of typically 40 MHz (0.001 33 cm^{-1}) are observed.

C. Electronic structure calculations

First, Conformer–Rotamer Ensemble Sampling Tool (CREST)¹⁷ calculations were performed to explore as exhaustively as possible the conformational landscape of the molecule. The CREST calculations procure a set of structures, which are then optimized using Gaussian 16 rev. C.01 software¹⁸ on the computing clusters of PhLAM laboratory. The frozen-core approximation was used throughout. Dunning and co-workers augmented correlation consistent basis set aug-cc-pVXZ ($X = \text{D, T, Q}$) were used (denoted aVDZ, aVTZ, and aVQZ).¹⁹ All geometries were fully optimized at the MP2 and B98 levels using the tight convergence criterion. The quadratic synchronous transit (QST2; as implemented in Gaussian software) was used to calculate the structure of the transition states (TS) between stable conformers. Frequencies and rotational constants in relevant vibrational states were calculated at the anharmonic level (VPT2 calculations as implemented in the Gaussian software)²⁰ with a tight SCF convergence criterion and the ultrafine integral grid option. Anharmonic corrections have

been extrapolated from DFT (B98) to the MP2 level following a method (denoted “hybrid”) suggested by Puzzarini *et al.* [see Eq. (86) in Ref. 21] and successful in the case of systems containing carbonyl groups.^{12,22,23} Extrapolations to complete basis set (CBS) for energies (including ZPE corrections), anharmonic frequencies, and rotational constants were performed from aVDZ, aVTZ, and aVQZ results using Dunning’s formula [see Eq. (1) in Ref. 24]. “hybrid” values were first calculated for each basis sets, then CBS extrapolations were performed on these hybrid/aVXZ (X = D, T, Q) values. In cases where CBS convergence is not satisfactory (i.e., aVXZ points do not show a correct exponential shape), values from the highest level (aVQZ) were used instead. Concerning rotational constants, once experimental GS values are known, calculated ES rotational constants values can be corrected from GS deviation (see Sec. IV B).

III. RESULTS

A. Conformational landscape

The CREST calculations resulted into 4 structures within 50 kJ mol^{−1}. MP2/aVQZ optimized structures (see Table S2 in [supplementary material](#)) and hybrid/CBS relative energies are displayed in Fig. 1. As expected for cyclohexane derivatives,²⁵ the chair structure is by far the most stable conformation. Two twisted boat structures are calculated to be stable conformers at relative energies higher than 26 kJ mol^{−1}, corresponding to negligible Boltzmann populations at room temperature (lower than 0.003%). The boat conformer is actually a TS between the two twisted boats. The QST2 calculations provide the high energy TS (around 50 kJ mol^{−1}) between the chair and the two twisted boats. Therefore, only the chair conformer is expected in the sample.

B. Vibrational analysis

DX is a slightly oblate asymmetric top rotor (Ray’s parameter $\kappa = 0.66$) belonging to the C_{2h} point group with 36 normal vibrational modes: 18 Raman-active (A_g and B_g) and 18 IR-active (A_u and B_u). In the present work, the most intense IR-active

vibrational bands of DX are observed in the fingerprint region (700–1500 cm^{−1}), as shown firstly from a low resolution (0.5 cm^{−1}) FTIR spectrum recorded with Jet-AILES (see Fig. 2). Vibrational assignments are based on both comparison with anharmonic frequencies obtained from two calculation methods (at the hybrid MP2/B98 level at the CBS limit and with the largest aVQZ basis set) and the dipole type consistent with the vibrational selection rules for the observed infrared transitions. Rotationally unresolved bands are clearly observed for the most intense fundamentals at 882.6, 1130.7, and 1257.4 cm^{−1}, with band shapes characteristic of *a/c*- and *b*-type transition dipoles and finally assigned to ν_{34} , ν_{16} , and ν_{15} modes, which have calculated anharmonic intensities (B98/aVQZ) greater than 35 km mol^{−1}. Despite an anharmonic intensity of 17 km mol^{−1}, the ν_{18} band (predicted about 8 cm^{−1} above ν_{34}) is not observed. Five weaker bands (intensities ≤ 10 km mol^{−1}) are unambiguously assigned to ν_{33} , ν_{17} , ν_{32} , ν_{14} , and ν_{30} modes using similar arguments: calculated anharmonic frequencies lie within ± 15 cm^{−1} of the experimental ones, and the presence (or absence) of narrow Q branches for ν_{33} , ν_{32} , and ν_{30} (and for ν_{17} , ν_{14}) indicates *a/c*-type (and *b*-type) transition dipoles in agreement with vibrational selection rules.

For the weak Q branches at 1293.6 and 1448.1 cm^{−1}, B_u symmetry vibrations are expected, which should exhibit a-type (or *a/c*-hybrid) band contours. Consequently, the ($\nu_{18} + \nu_9$) combination band of A_u symmetry predicted at 1306 cm^{−1}, which would yield a b-type contour, is discarded. The most probable assignments for the 1293.6 cm^{−1} feature are either the ($\nu_{34} + \nu_{10}$) or ($\nu_{34} + \nu_9$) combination band of B_u symmetry. The weak Q branch at 1448.1 cm^{−1} cannot be assigned to the ν_{13} band (predicted in this region but of A_u symmetry); suitable candidates are the ($\nu_{33} + \nu_{10}$) and ($\nu_{24} + \nu_{19}$) combination bands of B_u symmetry expected near 1450 cm^{−1} with an intensity of about 2 km mol^{−1}.

The full list of FT-mid IR vibrational bands observed, including symmetry, dipole type relative to C_{2h} point group symmetry, and experimental frequencies compared with anharmonic calculated values, is reported in Table I.

At high resolution, fundamental bands with calculated anharmonic intensities larger than 40 km mol^{−1} were targeted with the Jet-AILES setup to derive ground- and excited-state molecular

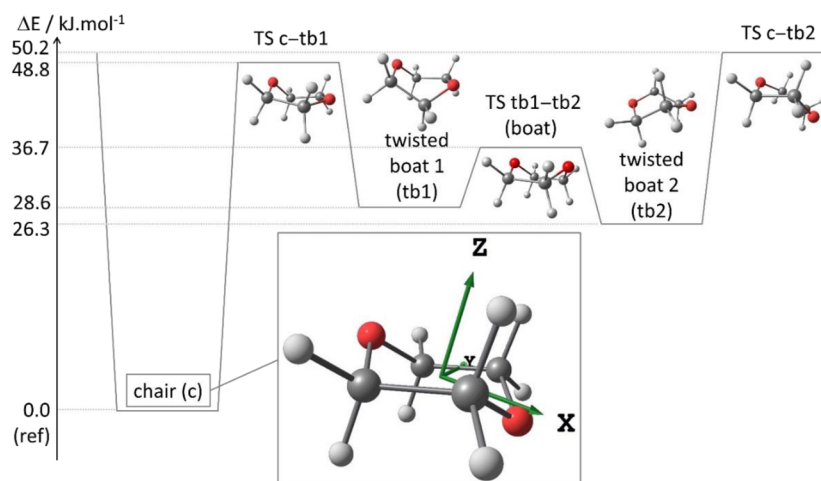


FIG. 1. Conformational landscape of DX. The zero point corrected relative energies, expressed in kJ/mol, are calculated at the hybrid/CBS level (see text for details).

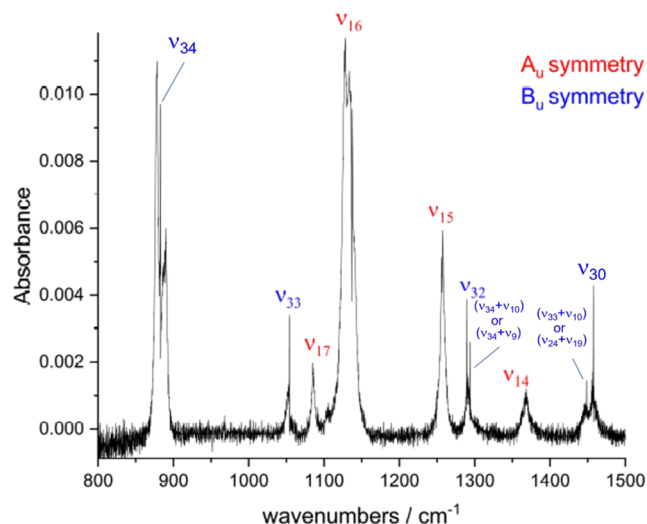


FIG. 2. Jet-AILES FT-mid-IR spectrum of 1,4-dioxane recorded at 0.5 cm^{-1} resolution shown over the $800\text{--}1500\text{ cm}^{-1}$ range. The vibrational assignments on the figure, with infrared active A_u and B_u symmetries are based on comparison with anharmonic calculations (see text for details).

parameters from the rovibrational analysis of the jet-cooled spectrum at 0.00102 cm^{-1} resolution. The targeted modes are associated with ring deformations in the ab plane (ν_{34} , ν_{16}) and CH_2 twisting (ν_{15}). For the SPIRALES setup, only the ν_{33} band at about 1054 cm^{-1} (anharmonic intensity: 9 km mol^{-1}) falls within the spectral range covered by the EC-QCLs available at MONARIS.

C. High resolution supersonic jet and long path cell measurements

Considering previous high-resolution studies of large organic molecules performed with Jet-AILES,^{12,26} the sensitivity of our jet-cooled IR absorption spectrometer proves sufficient to exploit the three rotationally resolved bands of DX targeted here (ν_{34} , ν_{16} , and ν_{15}), which have calculated anharmonic intensities of 70, 185, and 35 km/mol , respectively.

Rotational temperatures of about 50 K ¹² are typically attained for large molecules of similar molar mass under Jet-AILES supersonic expansion conditions (10% DX diluted in Ar with stagnation pressures $\sim 350\text{ hPa}$). Argon used as carrier gas in supersonic expansions is more efficient to cool down the molecule studied in our conditions of stagnation pressure and reduces the residual Doppler broadening by a factor 3 compared to helium. The Doppler width at 50 K for the three intense DX bands in the $850\text{--}1300\text{ cm}^{-1}$ range varies between 15 and 23 MHz ($0.0005\text{--}0.0008\text{ cm}^{-1}$). Consequently, Jet-AILES spectra are limited only by the apparatus function making essential to record them at maximal resolution to fully resolve the rotational structure.

Figure 3 displays the ν_{34} , ν_{16} , and ν_{15} bands of DX recorded at 0.00102 cm^{-1} resolution with Jet-AILES at low rovibrational temperature (black) and in the long path cell at 300 K (red). Figures 4–6 show zoomed parts of the Jet-AILES spectra on specific branches. The spectral simplification of the vibration–rotation bands due to rovibrational cooling in the supersonic expansion is evident on Fig. 3 from the narrowing of the rotational band contours, which is centered around $J'' = 15$ for the jet and $J'' = 40$ for the cell. Consequently, the SNR of rovibrational lines at low J'' , K''_a , and K''_c values is greatly increased in the jet spectra, facilitating the rovibrational analysis; by contrast, the Q branch of the ν_{34} band in the room-temperature cell spectrum is partially obscured by the high density

TABLE I. Vibrational mid-IR assignments of DX based on experimental measurements and anharmonic calculations at the hybrid/CBS and hybrid/aVQZ levels. All vibrational frequencies and intensities are given respectively in cm^{-1} and km mol^{-1} units.

ν_{exp}	Mode	Symmetry, dipole	Hybrid aVQZ	Hybrid CBS	$I_{\text{anharmonic}}^a$	Description
882.843 ^b	ν_{34}	$B_u, (ac)$ -type	883.6	886.1	69.2	ip ring deformation
...	ν_{18}	A_u, b -type	892.9	892.9	17.2	ip ring deformation
1053.971 ^b	ν_{33}	$B_u, (ac)$ -type	1051.5	1052.1	9.3	ip ring deformation
1085.2	ν_{17}	A_u, b -type	1089.3	1089.2	4.9	oop ring deformation
1136.668 ^b	ν_{16}	A_u, b -type	1140.2	1142.3	185.8	ip ring deformation
1256.738 ^b	ν_{15}	A_u, b -type	1259.0	1259.3	35.4	CH_2 twisting
1289.7	ν_{32}	$B_u, (ac)$ -type	1294.0	1294.1	10.1	CH_2 twisting
1293.6	$\nu_{34} + \nu_{10}$	$B_u, (ac)$ -type	1303.3	1305.1	1.3	...
	$\nu_{34} + \nu_9$		1310.6	1312.8	0.04	
1368.1	ν_{14}	A_u, b -type	1364.3	1361.3	4.8	CH_2 wagging
1448.1	$\nu_{33} + \nu_{10}$	$B_u, (ac)$ -type	1470.5	1470.3	2.1	...
	$\nu_{24} + \nu_{19}$		1477.1	1475.7	2.3	
1457.3	ν_{30}	$B_u, (ac)$ -type	1461.3	1458.1	8.3	CH_2 wagging

^aAnharmonic values at the B98/aVQZ level.

^bFrequencies of band centers for the excited states analyzed from high resolution experiments.

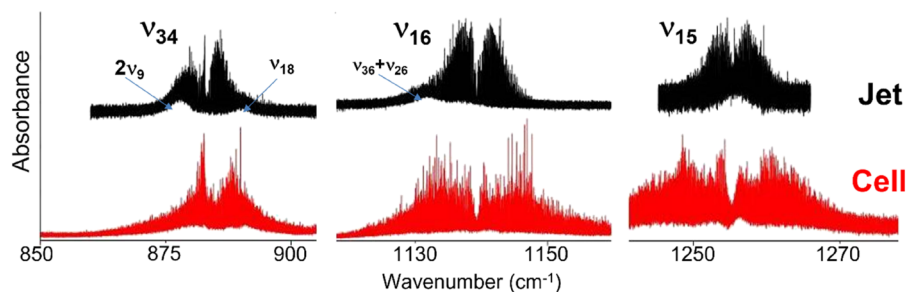


FIG. 3. ν_{34} , ν_{16} , and ν_{15} bands of 1,4-dioxane recorded with the Jet-AILES setup at low rovibrational temperature (black) and with the long-path cell at room temperature (red). Three broad unresolved features are clearly visible in the jet-cooled spectra relative to the ν_{34} and ν_{16} bands. They are tentatively assigned to the $(2\nu_9)$ overtone, ν_{18} , and the $(\nu_{36} + \nu_{26})$ combination bands.

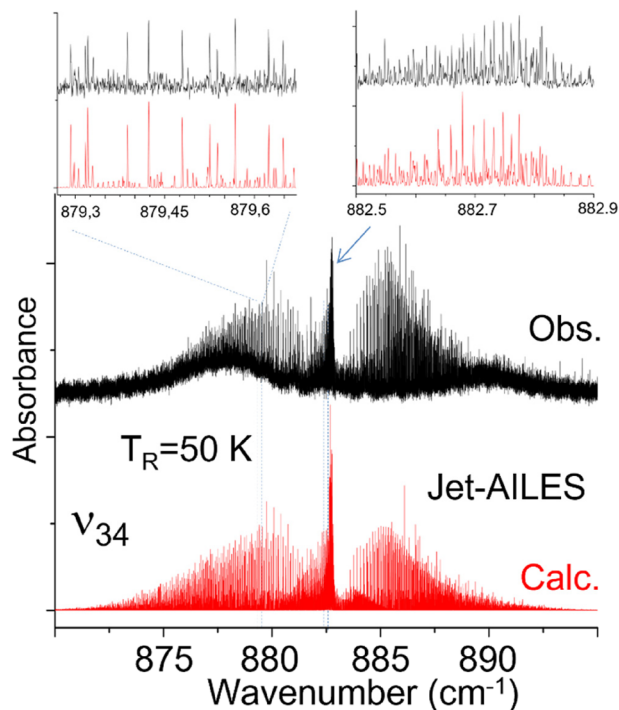


FIG. 4. Experimental ν_{34} band of 1,4-dioxane recorded with the Jet-AILES setup (black) and $\nu_{34} = 1 \leftarrow 0$ band simulated at a rotational temperature $T_R = 50$ K (red). The two insets display the resolved rotational structure of the P-branch (top left) and the Q-branch (top right). The distorted shape baselines are probably caused by the $(2\nu_9)$ overtone band and the broad ν_{18} perturbed band superposed on the P and R branches of the ν_{34} band.

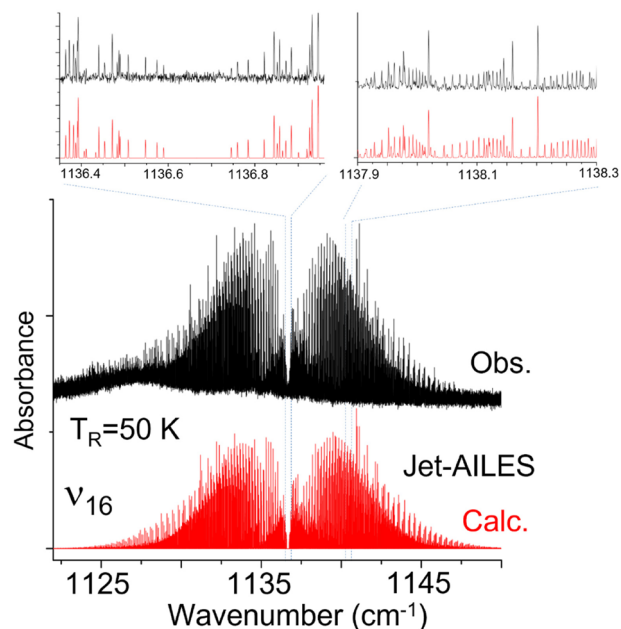


FIG. 5. Comparison of the experimental ν_{16} band of 1,4-dioxane recorded with the Jet-AILES setup (black) and the simulated $\nu_{16} = 1 \leftarrow 0$ transition at a rotational temperature $T_R = 50$ K (red). The two insets show the resolved rotational structure of the Q-branch (top left) and the R-branch (top right).

of overlapping lines. No hot band sequence involving the lowest frequency ring-bending modes ν_{19} and ν_{36} (calculated at 249 and 264 cm^{-1}) was observed, suggesting that integrated intensities of the first members of hot band sequences of the type $\nu_x + \nu_{36} \leftarrow \nu_{36}$ and $\nu_x + \nu_{19} \leftarrow \nu_{19}$ ($x = 34, 16, 15$) are reduced by about one order of magnitude between 300 and 100 K owing to rovibrational cooling and that ring-bending modes are weakly coupled to the in-plane ring deformation and CH_2 -twisting modes targeted here.

In the $870\text{--}900\text{ cm}^{-1}$ range, anharmonic calculations predict two observable bands: ν_{34} whose Q branch was observed at about 882.6 cm^{-1} in the low-resolution spectrum, and ν_{18} calculated to be about 3 times weaker and blue shifted from 6.8 to 9.3 cm^{-1} relative

to ν_{34} , according to the level of calculation (see Table I). The characteristic ν_{34} band contour is clearly visible in the Jet-AILES spectrum, with a Q branch centered at 882.75 cm^{-1} flanked by intense P and R branches, typical of an *a*-type band; however, there is no evidence of ν_{18} . Instead, in contrast with the flat baseline of the jet spectrum in the $860\text{--}905\text{ cm}^{-1}$ range, two broad, unstructured maxima centered near 877 and 890 cm^{-1} are observed beneath, both the P and R branches of ν_{34} . Since the spectrum was recorded at 0.00102 cm^{-1} resolution, these maxima cannot belong to the partially resolved rotational structure of ν_{34} . The most plausible candidates for the two broad features near the ν_{34} band are the $(2\nu_9)$ overtone and the ν_{18} fundamental bands (both of A_u symmetry), predicted near 857 and 893 cm^{-1} (B98/aVQZ), respectively. The calculated intensity of the ν_{18} band turns to be strongly overestimated due to its probable Coriolis coupling with ν_{34} . Similarly, the Jet-AILES spectrum in the $1122\text{--}1150\text{ cm}^{-1}$ range shows not only the characteristic

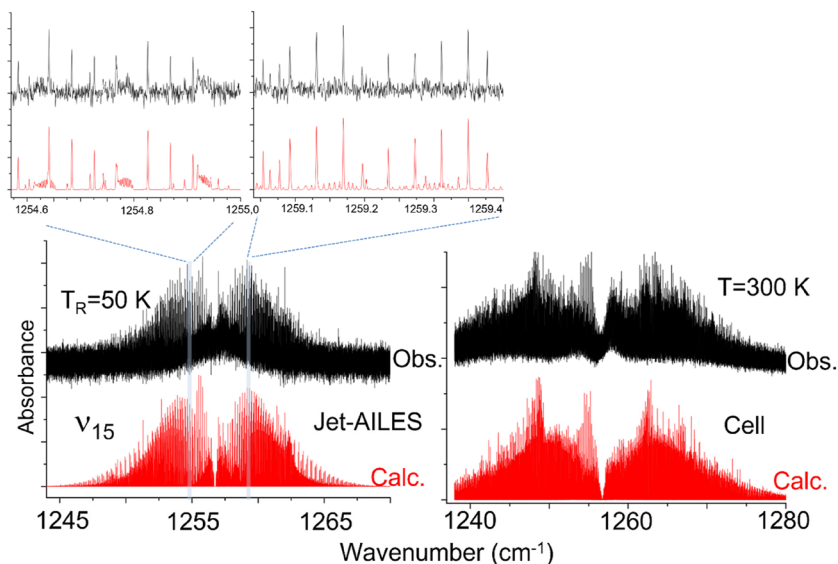


FIG. 6. Comparison of the experimental ν_{15} band of 1,4-dioxane with the simulated $\nu_{15} = 1 \leftarrow 0$ transition. Left: jet-cooled spectrum recorded with the Jet-AILES setup (black) and simulation at $T_R = 50$ K (red). Right: room-temperature long-path cell spectrum (black) and simulation at 300 K (red). The two insets show the resolved rotational structure of the P-branch (top left) and the R-branch (top right) under jet-cooled conditions.

b -type band contour of ν_{16} but also an unstructured maximum at 1127 cm^{-1} , on the high J level side of the P branch. Among the four combination bands predicted within $\pm 15\text{ cm}^{-1}$ around the ν_{16} band center, the $(\nu_{36} + \nu_{26})$ combination band of same A_u symmetry, calculated at 1130 cm^{-1} (hybrid/aVQZ) with an intensity of 5 km/mol (B98/aVQZ), is the most plausible candidate assignable to the broad feature observed and could be responsible for Fermi coupling with ν_{16} .

About the two other bands recorded at high resolution, no evident anomaly was observed: the b -type band contour of ν_{15} in the $1245\text{--}1270\text{ cm}^{-1}$ range displays the expected baseline for a high resolution rovibrational spectrum, with a symmetric bump centered under the Q branch due to the stronger density of lines in this region. Note that the density of vibrational states of same A_u symmetry within the $\pm 15\text{ cm}^{-1}$ range around ν_{15} is similar to that of ν_{16} , among them the $(\nu_{19} + \nu_7)$ combination band calculated at 1244 cm^{-1} with an intensity of 3 km/mol is a possible candidate for Fermi coupling.

Last, Fig. 7 displays the experimental jet-cooled spectrum of the ν_{33} band of B_u symmetry with a Q branch centered at 1053.9 cm^{-1} surrounded by intense P and R branches (*a/c* hybrid band type predicted by quantum calculations). Taking advantage of the high absorption sensitivity provided by pulsed expansions and multipass optics, lower rovibrational temperatures than in continuous expansions are achieved by injecting very diluted DX/Ar samples (1% DX in 2000 hPa Ar). The high-resolution cell spectrum of this weak band could not be exploited due to insufficient SNR. Only one very weak combination band was predicted within the $\pm 15\text{ cm}^{-1}$ range around ν_{33} .

D. Rovibrational analysis

Four bands of DX recorded at high resolution in the $860\text{--}1300\text{ cm}^{-1}$ range under jet-cooled conditions were analyzed to derive rotational parameters both for the ground state (GS) and the excited states $\nu_{34} = 1$, $\nu_{33} = 1$, $\nu_{16} = 1$, and $\nu_{15} = 1$. The simultaneous fit of the assigned transitions of four excited states is an

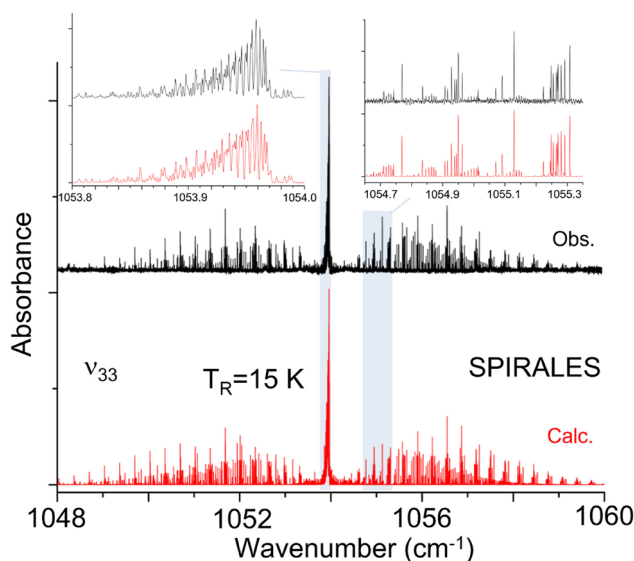


FIG. 7. Comparison of the experimental ν_{33} band of 1,4-dioxane recorded with the SPIRALES setup (black) and the simulated $\nu_{33} = 1 \leftarrow 0$ transition at a rotational temperature $T_R = 15$ K (red). The two insets show the resolved rotational structure of the Q-branch (top left) and the R-branch (top right).

efficient strategy to derive molecular parameters of centrosymmetric molecules provided that ground state rotational and quartic constants are released progressively to achieve a physical solution without correlations and changes in sign of distortion parameters.

Each band was first fitted individually using a Watson-type semirigid rotor model for slightly oblate asymmetric tops (A reduction in the III^1 representation) developed up to quartic centrifugal distortion (CD) terms with the PGOPHER program²⁷ and the SPFIT/SPCAT programs.²⁸ The ν_{16} and ν_{15} bands of A_u symmetry

give rise to *b*-type band contours, while for the ν_{34} and ν_{33} bands of B_u symmetry, (*a/c*) hybrid bands are expected. The effect of nuclear spin statistics was also considered: in the chair conformation, DX contains four pairs of identical protons that interchange with their partners under the C_2 operation of the C_{2h} point group. For exchange of an even number of fermion pairs, the total wavefunction must remain symmetric giving statistical weights for the GS levels equal to 17/17/15/15 for $K_a K_c = ee/oo/eo/oe$. This very small intensity alternation was included, although it was difficult to observe in our jet-cooled spectra.

GS rotational parameters were initially fixed to the experimental values of Den *et al.*¹¹ [$A'' = 5084.4(5)$ MHz, $B'' = 4684(1)$ MHz, $C'' = 2744.7(8)$ MHz, $\pm 1\sigma$ uncertainty] obtained by fitting the femtosecond RCS transients to an asymmetric-top model. GS quartic parameters were fixed to CCSD(T) calculated values of Den *et al.*¹¹ using quadruple zeta cc-pCVQZ basis sets. For each band, a preliminary fit was realized using PGOPHER program with all GS parameters fixed. ES rotational parameters were firstly adjusted by starting from MP2/AVQZ predictions corrected from the GS deviation. ES quartic constants were then adjusted progressively: if sign change occurs for a ES parameter, it is kept fixed to the GS one. Last, GS rotational constants are released to refine each individual simulation. Once the four preliminary fits realized, a global simulation using the SPFIT program was achieved by fixing the GS rotational parameters to averaged values derived from the four individual simulations. The first step was to refine progressively ES parameters of four bands by releasing firstly rotational then CD quartic ones. Finally, GS rotational and CD quartic constants are released successively. Such a procedure enabled to achieve a physical four-excited state fit by keeping the sign of ES CD quartic parameters unchanged with respect to the GS and without introducing ES CD sextic parameters.

The rovibrational analysis of the *a*-type ν_{34} band proved quite challenging: the Jet-AILES band spectrum was not reproduced when the calculated variations of rotational constants predicted by MP2/AVQZ hybrid methods ($\Delta A = -13.5$ MHz, $\Delta B = +0.4$ MHz, $\Delta C = -4.8$ MHz) are introduced into the simulation. By contrast,

the discrepancy between experimental and calculated line positions substantially decreases for large variations of the excited-state C' rotational ($\Delta C \approx -70$ MHz). The theoretical predictions of ES rotational constants are better in the case of the *b*-type ν_{16} band but for both bands, individual simulations with GS parameters fixed failed to adjust ES CD constants without sign changes. Only the constraints imposed on these parameters during the four-excited state fit enabled to alleviate this problem. Nevertheless, both fits of the ν_{34} and ν_{16} bands make appear large variations of ES CD quartic constants, which will be discussed hereafter. The rovibrational analysis of the *b*-type ν_{15} band was facilitated by the good SNR of the Jet-AILES spectrum. From the jet-cooled ν_{15} band spectrum of Brown *et al.*⁹ recorded at a lower rotational temperature (10 K), 55 new rovibrational lines (mainly with $J'' < 10$) were added to the list of FT lines. In a second step, CD quartic terms were refined thanks to the assignment of rovibrational lines with high J'' and K_a'' quantum numbers in the cell spectrum.

Last, the rovibrational analysis of the SPIRALES (*ac*)-type ν_{33} band was straightforward thanks to the high SNR of the pulsed jet-cooled spectrum, which reached much lower rotational temperatures compared to continuous supersonic jets, as shown by transitions only with J'' , K_a'' quantum numbers ≤ 18 and 11, respectively, so that it was not possible to adjust ES CD quartic constants.

In total, 6150 lines, of which 5043 were jet-cooled lines (including 34 lines of Brown *et al.*) and 1107 were RT lines of DX belonging to the four excited states $\nu_{34} = 1$, $\nu_{33} = 1$, $\nu_{16} = 1$, and $\nu_{15} = 1$, were fitted globally to instrumental accuracy. The root-mean-square (RMS) values of differences between observed and calculated frequencies are equal to 0.000 28 and 0.000 30 cm^{-1} , respectively, after applying the 3σ rejection criterion (where σ is the experimental precision fixed to 0.0005 cm^{-1} for jet-cooled lines and 0.0002 cm^{-1} for cell-FTIR lines). The GS and four ES rotational parameters are reported in Table II. Figures 4–7 compare experimental mid-IR spectra of the ν_{34} , ν_{16} , ν_{15} , and ν_{33} bands with their simulated jet-cooled spectra at rotational temperatures of 50 K (Jet-AILES) and 15 K (SPIRALES) and with the RT cell spectrum of the ν_{15} band (Fig. 6) using molecular parameters from the global fit. Table S1

TABLE II. Molecular parameters (MHz) for the ground state and the $\nu_{34} = 1$, $\nu_{33} = 1$, $\nu_{16} = 1$, and $\nu_{15} = 1$ excited states of DX, derived from the combined fit of five vibrational states.

Frequency (cm^{-1})	GS	ν_{34} 882.842 73(4)	ν_{33} 1053.971 10(2)	ν_{16} 1136.667 67(2)	ν_{15} 1256.737 55(2)
A	5084.264(15)	5067.729(29)	5059.887(20)	5073.064(22)	5079.084(17)
B	4685.039(14)	4685.223(26)	4686.478(19)	4686.202(17)	4682.585(16)
C	2744.265(6)	2671.068(10)	2736.383(9)	2744.137(7)	2741.153(7)
$\Delta_J (\times 10^3)$	1.145(10)	4.554(33)	1.145 ^a	0.458(14)	1.138(12)
$\Delta_K (\times 10^3)$	1.197(37)	1.457(107)	1.197 ^a	1.091(57)	1.252(40)
$\Delta_{JK} (\times 10^3)$	-1.989(43)	-24.11(14)	-1.989 ^a	-1.200(39)	-2.004(48)
$\delta_J (\times 10^3)$	0.063(9)	0.794(26)	0.063 ^a	2.064(16)	0.079(8)
$\delta_K (\times 10^3)$	0.51(17)	76.09(40)	0.51 ^a	2.34(26)	0.63(19)
RMS	...	10.5	9.7	9.2	9.0
N lines	...	1107	989	2266	1788
J''	...	1–44	1–18	1–54	1–47
K_a''	...	0–25	0–11	0–53	0–47

^aQuartic constants fixed to ground state values.

containing line assignments, measured frequencies, uncertainties, and deviations is provided in the [supplementary material](#).

IV. DISCUSSION

A. Reliability of high-resolution parameters

Taking advantage of the broad spectral coverage of high-resolution FTS, four bands of DX were recorded and analyzed, yielding a set of GS and ES molecular parameters from the assignment of more than 6100 lines fitted to the experimental accuracy.

However, the reliability of these parameters, particularly the ground state values, may be questioned because of a presumed Coriolis-type perturbation between ν_{34} (B_u symmetry) and ν_{18} (A_u symmetry), evidenced by the near extinction of the ν_{18} band intensity, likely due to rovibrational line broadening. This argument is supported by the presence of a broadband around 890 cm^{-1} that correlated with anharmonic frequency calculations. A second broad line feature around 877 cm^{-1} , tentatively assigned to the $(2\nu_9)$ overtone (A_u symmetry), could also perturb the fundamental band. Although the perturbed bands identified in the DX spectrum all exhibit an unresolved structure, this is not always the case: in a

recent paper on nitrogen-substituted PAHs,²⁹ several isoquinoline bands—strongly perturbed by Coriolis interactions—retain a fully (or partially) resolved rovibrational structure in most cases. This hypothesis of Coriolis perturbation is supported by the strong variations observed for several ν_{34} molecular parameters: $\Delta C = -73\text{ MHz}$ (about 2.5% decrease vs GS) and the increase in several ES CD quartic parameters, such as Δ'_j , Δ'_{JK} , δ'_j , and δ'_K by factors equal to 4, 12, 12, and 150, respectively. The probable presence of the $(\nu_{36} + \nu_{26})$ combination band around 1127 cm^{-1} , superposed on the P branch of the ν_{16} band, may explain why several tens of $^P P(^R R)$ transitions with $J'' = K''_a \geq 15$ and $K''_c = 1(0)$ are shifted by up to few tenths of a wavenumber from the asymmetric top model, which should be, therefore, discarded. The variations of ES CD quartic parameters for ν_{16} although higher than expected for an unperturbed vibration (Δ'_j , Δ'_{JK} , δ'_j , and δ'_K multiplied by 0.4, 0.6, 30, and 4.5) are largely weaker compared to those observed for ν_{34} . Finally, both analyses of ν_{33} and ν_{15} bands turn to be straightforward, with very few unassigned lines. The very small variations of ES CD quartic parameters for ν_{15} seem to indicate the absence of effective vibrational perturbors in this region [despite the close presence of the $(\nu_{19} + \nu_7)$ combination band], while for ν_{33} , the quasi absence of

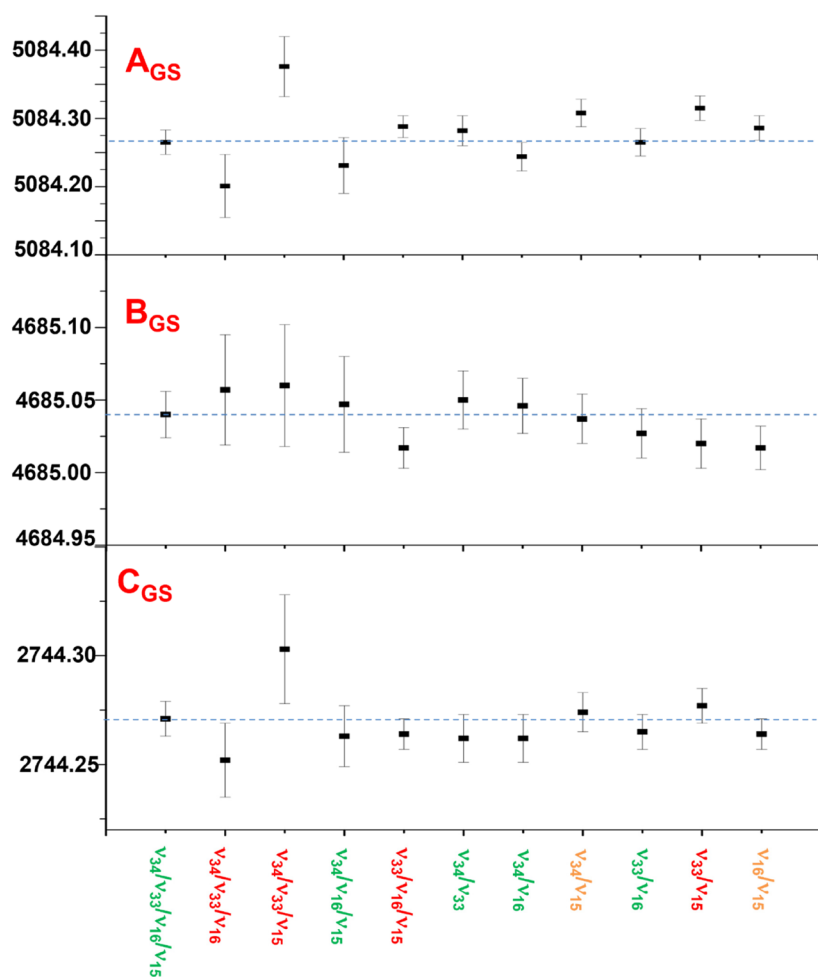


FIG. 8. Comparison of GS rotational constants (MHz) from the four-state global fit with those from four three-state fits and six two-state fits (shown left to right) involving the ν_{34} , ν_{33} , ν_{16} , and ν_{15} bands of DX. The blue dotted lines show the GS rotational constants from the full fit including the 4 bands, used as reference values for the 2- and 3-state fits. The error bars are the RMS of the differences between observed and calculated frequencies after applying the 3σ rejection criterion. The color code for fit quality is defined in the text.

combination bands near its band center is coherent with the absence of sign perturbation. Recall that an in-depth line-by-line analysis of rotation–vibration couplings evidenced here is out of reach for such highly excited states. Only room temperature millimeter-wave experiments enable to treat in detail these interactions in the far-IR range with the suitable sub-MHz resolution. In the mid-IR range, we could only propose possible candidates as vibrational perturbers that typically behave as dark states (no resolved structure or too weak to be detected) as is the case in the present rovibrational study.²⁹

To evaluate the possible effect of these perturbations on the GS parameters derived here, different combinations of rovibrational simulations were performed using only two or three bands of the four analyzed ones. The aim was also to check whether the accuracy obtained of the molecular parameters is correlated with the widest accessible set of dipole moment projections in global fits [mainly, *a*-type and hybrid (*-ac*) bands for the ν_{34} and ν_{33} in plane ring modes, respectively, and *b*-type bands for the ν_{16} and ν_{15} CH₂ twisting vibrations] or with other factors such as band intensity or rovibrational simulation. Strong constraints on band positions are expected when different selection rules for the parities of ΔK_a and ΔK_c apply, which should reduce correlations among rovibrational transitions and, thus, improve precision of the ground state parameters.

Figure 8 shows the three GS rotational constants with error bars derived from four combinations of three-state fits ($\nu_{34}/\nu_{33}/\nu_{16}$, $\nu_{34}/\nu_{33}/\nu_{15}$, $\nu_{34}/\nu_{16}/\nu_{15}$, $\nu_{33}/\nu_{16}/\nu_{15}$) and six combinations of two-state fits (ν_{34}/ν_{33} , ν_{34}/ν_{16} , ν_{34}/ν_{15} , ν_{33}/ν_{16} , ν_{33}/ν_{15} , ν_{16}/ν_{15}) compared with the global four-state fit (ν_{34} , ν_{33} , ν_{16} , ν_{15}). Among these ten fits, four ($\nu_{34}/\nu_{33}/\nu_{16}$, $\nu_{34}/\nu_{33}/\nu_{15}$, $\nu_{33}/\nu_{16}/\nu_{15}$, ν_{33}/ν_{15} shown in red) yield the largest shifts from the global values: $\Delta A = 0.06(4)$ MHz, $\Delta B = 0.020(2)$ MHz, and $\Delta C = 0.016(12)$ MHz. Two fits (ν_{34}/ν_{15} , ν_{16}/ν_{15} —orange) produce smaller deviations and similar error bars to the global fit. Finally, four fits ($\nu_{34}/\nu_{16}/\nu_{15}$, ν_{34}/ν_{33} , ν_{34}/ν_{16} , ν_{13}/ν_{16} —green) give the most consistent GS constants with error bars compatible with the global fit.

From these observations, it seems evident that none of the four modes should be discarded from the global fit. In particular, the ν_{34} mode contributes to the best fits, which proves that its probable involvement in Coriolis interactions has no consequence on the GS rotational parameters. Whatever the number and the vibrational modes used for the excited-state fits, the final set of GS rotational constants varies remarkably little. No correlation is observed between the presence of modes in the “best” fits and their calculated anharmonic intensities. The weaker intensity of the ν_{33} band (9 km/mol) is largely compensated by the higher sensitivity

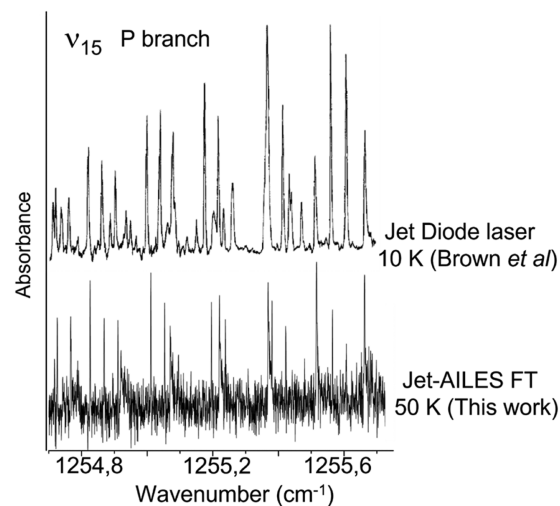


FIG. 9. Comparison between the jet-cooled spectrum obtained using FTS at 0.001 cm^{−1} resolution (Jet-AILES spectrum, bottom) and the pulsed jet-cooled spectrum using IR diode laser spectroscopy (Brown *et al.*⁹ top) in the P branch region of the ν_{15} band of DX. The strong broadenings of rotational lines observed in the pulsed jet are probably due to non-orthogonal crossings between the molecules expanded from the circular expansion and the IR laser light.

of the SPIRALES setup. Instead, the lower rotational temperature (15 K) inferred from the ν_{33} jet-cooled spectrum prevents reliable determination of CD quartic constants, which were, therefore, fixed to GS values; this approximation could slightly impact the precision of GS and ES rotational constants, as observed for the three-state fits ($\nu_{34}/\nu_{33}/\nu_{16}$) and ($\nu_{34}/\nu_{33}/\nu_{15}$) involving ν_{33} (Fig. 8). Finally, no significant difference was found between the partial fits involving only *b*-type bands (ν_{16}/ν_{15}) and mixed *a*- and *b*-type bands (ν_{34}/ν_{16} , ν_{34}/ν_{15}), indicating that choosing modes with different dipole-moment projections is not the decisive factor for fit quality in the present HR jet-cooled and cell IR spectra.

Table III gathers the GS and $\nu_{15} = 1$ rotational constants derived from this work and previous studies. The GS constants from the Raman RCS study of Den *et al.*¹¹ are quite compatible with ours, but the global fit of four-excited vibrational states probed in jet-cooled conditions at high resolution provides reliable molecular parameters with a largely improved precision by more than two

TABLE III. Comparison of the ground state and $\nu_{15} = 1$ molecular parameters of DX from previous fs Raman RCS gas-cell and IR diode-laser jet studies with those from the present work (in boldface).

	Ground state			$\nu_{15} = 1$	
	This work	fs-Raman RCS gas cell ¹¹	IR diode laser jet ⁹	This work	IR diode laser jet ⁹
A	5084.264(15)	5084.4(15)	5084.81(90)	5079.084(17)	5080.16(90)
B	4685.039(14)	4684(3)	4685.79(90)	4682.585(16)	4683.21(90)
C	2744.265(6)	2744.7(24)	2744.39(36)	2741.153(7)	2741.39(36)

orders of magnitude. The GS constants derived from the IR diode laser jet study of Brown *et al.*,⁹ based on a one-excited state fit (v_{15}), are compatible with GS data of Den *et al.*¹¹ as well as our results but with a lesser precision by a factor of about 60, due to several reasons: (i) their rovibrational analysis is based on the simulation of 136 lines of which only 42 ones were given with heavier weight; (ii) the estimated uncertainty of DX line positions is relatively large (0.0025 cm^{-1}) because of strong Doppler broadening in their axisymmetric supersonic expansion (Fig. 9) as evidenced by the large (obs. - calc.) residuals reported in their tables and also the rejection of 20 lines of Brown *et al.*'s⁹ according to our criterion (0.0005 cm^{-1}) among 55 new ones added in the four-excited state fit (Table S1), (iii) although the diode laser jet spectrum has better SNR than the jet-cooled FT spectrum, the very low rotational temperature in the pulsed jet (15 K) prevents precise determination of CD quartic constants, which—as noted above—reduces the accuracy of the derived rotational constants.

B. Comparison between theoretical and high-resolution experimental parameters

As already mentioned in previous studies, theoretical predictions using the present methodology for vibrational frequencies are accurate in the order of tenth of %, resulting in largest errors of few tens of cm^{-1} . However, these rough predictions are sufficient to assign observed vibrational bands. A total of 10 experimental frequencies, including 2 combination bands, were observed and assigned (Table I), based on predictions with a mean absolute error (MAE) of the differences between experimental and calculated values of 5.8 and 6.3 cm^{-1} for hybrid/aVQZ and hybrid/CBS, respectively, which correspond to a mean relative error around 0.45% . Table S3 and S4 containing all calculated frequencies and intensities for fundamental bands are provided in the [supplementary material](#).

The GS- and ES-calculated rotational constants at the hybrid/aVQZ and hybrid/CBS levels are compared with the experimental molecular parameters derived from high resolution measurements of DX in Table IV. Two differences, namely $\delta_{\text{aVQZ}} = \text{exp} - \text{hybrid/aVQZ}$ and $\delta_{\text{CBS}} = \text{exp} - \text{hybrid/CBS}$, are reported together with the differences $\delta_{\text{corr_aVQZ}}$ and $\delta_{\text{corr_CBS}}$ calculated using ES theoretical values corrected from the GS deviation according to the expression $X_v^{\text{corr}} = \frac{X_v^{\text{calc}} \times X_{\text{GS}}^{\text{exp}}}{X_{\text{GS}}^{\text{calc}}}$ where $X = A, B, C$.³⁰ Except for the C constant of the $v_{34} = 1$ state for which δ_{corr} values are near -70 MHz , the corrected differences between calculated and experimental rotational constants are reasonable and consistent with previous studies,¹² yielding similar MAEs of 0.95 MHz for the 11 other constants predicted by both hybrid methods.

Comparing this parameter across excited states shows a clear correlation between the magnitude of the corrected MAEs, 23.9 , 0.9 , 1.1 , and 0.3 MHz for $v_{34} = 1$, $v_{33} = 1$, $v_{16} = 1$, and $v_{15} = 1$, respectively, and the vibrational perturbations suggested from the high-resolution band contours observed and then evidenced from our rovibrational analyses. It highlights the usefulness of the calculations in qualitatively assessing for the presence of a vibrational perturbation, in addition to the unambiguous assignment of the observed bands. Quantitatively, the accuracy of such calculations (few MHz) is not enough to correctly produce a synthetic spectrum within HR spectroscopy standards (few kHz), but increasing the accuracy often finds its limit in the computational cost. Ultra-high level calculations with extended basis sets can simulate the HR spectrum of small molecules,³¹ but they are computationally out of reach for DX. The present case of DX shows again that the hybrid method offers the best compromise, greatly improving the accuracy compared to direct anharmonic calculations at the MP2 or DFT levels, at a reasonable computational cost: (opt + freq) at MP2/aVQZ and (opt + anarm) at B98/aVQZ ran in about 420 h on 24 procs.

TABLE IV. Deviation ($\delta = \text{exp} - \text{calc}$) of the rotational constants for the ground and excited states of DX for both hybrid calculation methods (with aVQZ basis set and at the CBS limit).

		Experimental	Calculated		$\delta = \text{exp} - \text{calc}$		δ corrected from GS deviation	
			Hybrid/CBS	Hybrid/aVQZ	δ_{CBS}	δ_{aVQZ}	$\delta_{\text{corr_CBS}}$	$\delta_{\text{corr_aVQZ}}$
GS	A	5084.264	5103.403	5094.144	-19.139	-9.880		
	B	4685.039	4692.014	4680.545	-6.975	4.494		
	C	2744.265	2753.090	2747.406	-8.825	-3.141		
v_{34}	A	5067.729	5089.980	5080.623	-22.261	-12.894	-3.162	-3.040
	B	4685.223	4692.459	4680.935	-7.226	4.288	-0.260	-0.206
	C	2671.068	2748.308	2742.579	-77.240	-71.511	-68.430	-68.375
v_{33}	A	5059.887	5080.795	5071.630	-20.908	-11.743	-1.854	-1.907
	B	4686.478	4692.977	4681.474	-6.499	5.004	0.478	0.509
	C	2736.383	2745.695	2739.971	-9.312	-3.588	-0.511	-0.456
v_{16}	A	5073.064	5092.297	5083.022	-19.233	-9.958	-0.136	-0.099
	B	4686.202	4696.136	4684.952	-9.934	1.250	-2.952	-3.248
	C	2744.137	2753.042	2747.406	-8.905	-3.269	-0.080	-0.128
v_{15}	A	5079.084	5098.186	5088.958	-19.102	-9.874	0.018	-0.004
	B	4682.585	4689.910	4678.416	-7.325	4.169	-0.353	-0.323
	C	2741.153	2750.470	2744.768	-9.317	-3.615	-0.500	-0.477

Moreover, reaching the CBS limit does not perform better than a single calculation with a sufficiently large basis set (aVQZ). Although such calculations cannot synthesize a spectrum at HR spectroscopy standards, they provide a realistic initial set of molecular constants, making it possible to analyze a complex laboratory spectrum.

V. CONCLUSION

An extensive high resolution IR spectroscopic study of DX, which combines jet-cooled and room-temperature measurements complemented by anharmonic quantum chemical calculations, was performed to measure precisely the rovibrational parameters of four vibrational bands in the fingerprint region. In the absence of a permanent dipole moment, ground- and excited-state parameters could be globally fitted to reproduce at the experimental accuracy the frequency of 6150 experimental lines belonging to the ν_{34} , ν_{33} , ν_{16} , and ν_{15} modes in the mid-IR range, yielding the most reliable set of molecular parameters of DX reported to date. Compared with previous gas-phase structural studies based on femtosecond Raman RCS and jet-cooled IR diode laser measurements, a markedly improved precision was achieved for GS and ES rotational constants, particularly for the ν_{15} mode. The robustness of the derived molecular parameters was obtained thanks to a step-by-step fitting procedure for which the rotational and CD quartic parameters of the ground state (treated as it were a dark state) were initially fixed to experimental (rotational constants) and calculated using highly correlated coupled-cluster method and cc-pCVXZ basis-set series (CD quartic constants) from the reference study of Den *et al.*¹¹ The refinement of the ES parameters roughly determined from individual fits was then realized from a four-excited state fit enabling to introduce some indirect constraint as all measured transitions originate from the ground vibrational state. The reliability of the global fit was confirmed through an in-depth examination of different combinations of two- and three-excited state fits, showing that the four vibrational states involved in this study do not introduce any bias in the rovibrational analyses, despite a probable Coriolis coupling between ν_{34} and ν_{18} fundamental bands and possibly at a much lesser extent, an eventual Fermi coupling between ν_{16} and a close combination band. The study highlights the critical role of high SNR jet-cooled spectra in achieving precise molecular parameters and demonstrates the strong complementarity between broadband Fourier transform spectroscopy and laser-based techniques.

The resulting dataset, including accurate line positions and molecular constants, provides a solid foundation for the sensitive and selective detection of 1,4-dioxane in the atmosphere. As demonstrated for the ν_{15} fundamental band (Fig. 6), the precise line list generated in this work allows for the accurate simulation of DX rovibrational spectra across a wide temperature range in the fingerprint region. This quantum mechanical template provides a powerful tool to refine existing public databases, such as HITRAN³² or PNNL,³³ where available DX cross sections are based on medium-resolution FTIR measurements ($\geq 0.1 \text{ cm}^{-1}$) that cannot resolve the rotational structure. Following the methodology recently validated on furfural,¹² our high-resolution line lists enable the precise isolation and quantification of room-temperature hot bands from the unresolved experimental envelopes. Accounting for these hot bands, which freeze out at lower temperature, is critical for generating accurate temperature-dependent synthetic cross-sections. This

work, thus, underscores the importance of high-resolution laboratory spectroscopy in improving forward models for remote sensing and monitoring emerging contaminants within the 8 to 14 μm atmospheric transparency window.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) file contains 4 data tables: Table S1 provides line assignments, measured frequencies, uncertainties, and deviations related to the global rovibrational analysis. Table S2 gathers the principal axis Cartesian coordinates of 1,4 DX conformers calculated at the MP2/aug-cc-pVQZ level. Table S3 gathers the full list of harmonic frequencies (in cm^{-1}) and intensities (in km/mol) calculated at the MP2 level. Table S4 gathers the full list of harmonic frequencies (in cm^{-1}) and intensities (in km/mol) calculated at the B98 level.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Pierre Asselin: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Software (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jordan A. Claus:** Investigation (equal); Writing – review & editing (equal). **Colwyn Bracquart:** Investigation (equal); Writing – review & editing (equal). **Manuel Goubet:** Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Olivier Pirali:** Investigation (equal); Writing – review & editing (equal). **Robert Georges:** Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Arnaud Cuisset:** Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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