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Rotationally resolved infrared spectroscopy of adamantane

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We present the first rotationally resolved spectra of adamantane ($C_{10}H_{16}$) applying gas-phase Fourier transform infrared (IR) absorption spectroscopy. High-resolution IR spectra are recorded in the 33–4500 cm^{-1} range using as source of IR radiation both synchrotron radiation (at the AILES beamline of the SOLEIL synchrotron) as well as a classical globalar. Adamantane is a spherical top molecule with tetrahedral symmetry (T_d point group) and has no permanent dipole moment in its vibronic ground state. Of the 72 fundamental vibrational modes in adamantane, only 11 are IR active. Here we present rotationally resolved spectra for seven of them: ν_{30} , ν_{28} , ν_{27} , ν_{26} , ν_{25} , ν_{24} , and ν_{23} . The typical rotational structure of spherical tops is observed and analyzed using the STDS software developed in the Dijon group, which provides the first accurate energy levels and rotational constants for seven fundamental modes. Rotational levels with quantum numbers as high as $J = 107$ have been identified and included in the fit leading to a typical standard deviation of about $10^{-3} cm^{-1}$.

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I. INTRODUCTION

As the smallest building block of the series of diamondoid molecules, adamantane ($C_{10}H_{16}$) is a molecule of fundamental interest, comparable for instance to benzene as the progenitor of polyaromatic species or methane as the progenitor of simple alkanes. Adamantane belongs to the family of cyclo-alkanes and represents a single cage of a diamond lattice. It consists of a single, fully aliphatic tetrahedral carbon cage (see Fig. 1) where all carbon atoms are sp^3 hybridized and dangling bonds are terminated with hydrogen atoms. As most progenitor molecules, adamantane is a molecule with high symmetry, in fact belonging to the T_d point group.

Based on Meerwein's earlier attempts, Prelog was the first to synthesize adamantane,¹ although the process was complicated and the yield was low. In 1957, von Ragué-Schleyer found an alternative, much more efficient synthetic route to produce adamantane,² which launched the widespread application of the molecule and many of its derivatives, particularly in the areas of polymer chemistry, nanotechnology and medicine. In addition to these applications, adamantane and in particular higher diamondoid molecules have been hypothesized to occur in circumstellar environments, based on their vibrational signatures^{3–9} as well as on samples taken from the Murchinson meteorites.^{10–13}

Various researchers have investigated the spectroscopic properties of adamantane and other diamondoid molecules.

Vibrational spectra are available for adamantane,^{14–16} various larger diamondoid molecules¹⁷ including some of their positively charged ions^{18,19} and diamond nanoparticles.^{4,20} Adamantane displays strong Raman activity and Raman spectra of adamantane¹⁶ as well as of several larger diamondoid molecules^{21,22} have been reported. Similar to bulk diamond, diamondoid molecules including adamantane are widely transparent across the visible and UV parts of the spectrum and UV transitions are observed only beyond ≈ 6 eV (≈ 205 nm); synchrotron sources have been utilized to characterize the UV properties of a series of diamondoid molecules.²³ Furthermore, chiral properties of higher diamondoid molecules, as well as of halogenated adamantane have been studied with optical rotation and vibrational circular dichroism (CD and VCD) spectroscopy.^{24,25} Since adamantane is a tetrahedral molecule, it has no permanent dipole moment in its vibronic ground state, so that no pure rotational spectrum exists; moreover, to our knowledge, rotationally resolved IR or UV/vis spectra have not been reported to date for any diamondoid molecule, so that no experimental information on the rotational structure is available whatsoever.

In the present contribution, we report the first high-resolution, i.e., rotationally resolved, infrared spectra of adamantane. Out of the 72 vibrational modes (for which an assignment can be found in Refs. 14 and 16), only 11 triply degenerate F_2 modes are infrared active from the ground vibrational state (GS symmetry A_1). Of the 11 IR active bands, we were able to resolve the rotational structure of 7 of them, providing accurate energy levels for this molecule. As adamantane is a spherical top, the upper state rotational levels split in three components (indicated as F_2^+ , F_2^0 , and

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FIG. 1. Calculated structure of adamantane $C_{10}H_{16}$ obtained using the B3LYP density functional at the 6-31G(d,p) level of theory.

F_2^-) through “first order” Coriolis interaction. Finer effects, such as centrifugal distortion and Coriolis interactions with other vibrational states, split each component in a number of sub-levels indicated as *A*, *E*, and *F* (see, e.g., Ref. 26 for a general description of the rotational structure of spherical tops). Some bands show fully resolved clusters of lines in the *P*- and *R*-branches caused by the splitting of the energy levels corresponding to the *A*, *E*, and *F* components.

Finally, adamantane constitutes an excellent test for the tensorial formalism^{27,28} that has originally been developed for much smaller tetrahedral or octahedral molecules, such as methane and sulfur hexafluoride. $C_{10}H_{16}$ appears to be the biggest spherical-top molecular system ever studied at high resolution. Previously, the biggest system that was investigated with the tensorial model developed in the Dijon group was molybdenum hexacarbonyl, $Mo(CO)_6$, for which a single fundamental band has been modelled.^{29,30} Adamantane thus offers a unique opportunity to apply these models to multiple vibrational bands, possibly with some interactions between some of them.

II. METHODS

A. Experiment

All spectra in the 33–4500 cm^{-1} range have been recorded using a high-resolution Bruker IFS 125 inter-

ferometer located at the AILES beamline of the SOLEIL synchrotron facility. Gas-phase adamantane (99.5 % from Aldrich), was injected in a multipass cell of which the optics (White-type arrangement) were set to obtain a 151.75 m long absorption path. ZnSe windows (0.5° wedge, 5 mm thickness) separated the cell from the interferometer. Since the IR bands of adamantane possess relative intensities ranging from a few 10^{-2} $km\ mol^{-1}$ (e.g., the cage deformation mode at 400 cm^{-1}) to several hundreds of $km\ mol^{-1}$ (for the CH stretching modes in the 3 μm region), our spectra were recorded at different adamantane pressures and we used two different continuum sources to optimize the signal to noise ratio of the bands. Table I shows the different experimental conditions used to record three spectra covering the 33–4500 cm^{-1} spectral range. The three spectra have been recorded with a spectral resolution of 0.001 cm^{-1} . All bands except ν_{23} and ν_{30} have been recorded using a global continuum source together with an MCT detector and a KBr beamsplitter. In the first spectrum (600–4500 cm^{-1}) the gas pressure was set to about 0.05 mbar (in order to optimize the detection of the ν_{28} mode) and the acquisition time was about 24 h. In the second spectrum (33–600 cm^{-1}) we have made use of the SOLEIL synchrotron FIR radiation extracted by the AILES beamline as the continuum source of the FT interferometer, resulting in a significant improvement of the signal-to-noise ratio in comparison with the global source.^{31–34} For this experiment, the ring current was 300 mA in a “top-up” mode. The FTIR spectrometer was equipped with a He-cooled bolometer detector and a 6 μm mylar beamsplitter. Polypropylene films of 50 μm thickness were used as cell windows. We injected the maximum vapor pressure attainable at room temperature (about 0.1 mbar) to detect and rotationally resolve the weak ν_{30} band. Finally in the third spectrum (1000–2000 cm^{-1}), the intense ν_{28} mode has been recorded with a pressure of 0.01 mbar using the synchrotron source, KBr beamsplitter and MCT detector.

The peak finder available in the Bruker OPUS software was used and line positions were calibrated using lines of the ν_2 band of water³⁵ for the two mid-IR spectra and pure rotational water lines for the FIR spectrum.³⁶ The line frequency accuracy depends on the spectral region studied and on the signal to noise ratio of the band studied; however, for reasons of conformity, we adopt a fixed experimental uncertainty of 0.0002 cm^{-1} over the full IR range, which is a reasonable compromise for all bands.

B. Theory

$C_{10}H_{16}$ is a spherical top molecule with tetrahedral symmetry. Hence, its equilibrium geometry pertains to the

TABLE I. Experimental conditions.

Dataset	Spectral range	Gas pressure	Spectral resolution	Continuum source	Acquisition time
1	600–4500 cm^{-1}	0.05 mbar	0.001 cm^{-1}	global	24 h
2	33–600 cm^{-1}	0.1 mbar	0.001 cm^{-1}	synchrotron	24 h
3	1000–2000 cm^{-1}	0.01 mbar	0.001 cm^{-1}	synchrotron	8 h

T_d point group. Theoretical tools and programs already developed for other tetrahedral molecules such as CH_4 can thus be used for adamantane.

The theoretical model described below to develop the Hamiltonian operator is based on the tensorial formalism and vibrational extrapolation methods used in Dijon. These methods have already been explained for example in Champion *et al.*²⁷ and Boudon *et al.*²⁸ We only recall here the basic principles and their application to the case of a tetrahedral molecule.

If we consider an $\text{X}_{10}\text{Y}_{16}$ molecule for which the vibrational levels are grouped into a series of polyads designated by P_k ($k = 0, \dots, n$), P_0 being the ground state (GS), the Hamiltonian operator can be put in the following form (after performing contact transformations):

$$\mathcal{H} = \mathcal{H}_{\{P_0 \equiv \text{GS}\}} + \mathcal{H}_{\{P_1\}} + \dots + \mathcal{H}_{\{P_k\}} + \dots + \mathcal{H}_{\{P_{n-1}\}} + \mathcal{H}_{\{P_n\}}. \quad (1)$$

Terms such as $\mathcal{H}_{\{P_k\}}$ contain rovibrational operators which have no matrix elements within the $P_{k' > k}$ basis sets. The effective Hamiltonian for polyad P_n is obtained by projecting $\mathcal{H}$ in the P_n Hilbert subspace, i.e.,

$$\begin{aligned} H^{(P_n)} &= P^{(P_n)} \mathcal{H} P^{(P_n)} \\ &= H_{\{\text{GS}\}}^{(P_n)} + H_{\{P_1\}}^{(P_n)} + \dots + H_{\{P_k\}}^{(P_n)} + \dots + H_{\{P_{n-1}\}}^{(P_n)} + H_{\{P_n\}}^{(P_n)}. \end{aligned} \quad (2)$$

The different terms are written in the form

$$\mathcal{H}_{\{P_k\}} = \sum_{\text{all indexes}} t_{\{s\}\{s'\}}^{\Omega(K, n\Gamma)\Gamma_v \Gamma'_v} \beta [\varepsilon V_{\{s\}\{s'\}}^{\Omega_v(\Gamma_v \Gamma'_v)\Gamma} \otimes R^{\Omega(K, n\Gamma)}]^{(A_1)}. \quad (3)$$

In this equation, the $t_{\{s\}\{s'\}}^{\Omega(K, n\Gamma)\Gamma_v \Gamma'_v}$ are the parameters to be determined, while $\varepsilon V_{\{s\}\{s'\}}^{\Omega_v(\Gamma_v \Gamma'_v)\Gamma}$ and $R^{\Omega(K, n\Gamma)}$ are vibrational and rotational operators of respective degree Ω_v and Ω . Their construction is described in Ref. 27. Again, the vibrational operators only have matrix elements within the $P_{k' \leq k}$ basis sets. β is a factor that allows the scalar terms ($\Gamma = A_1$) to match the usual terms like $B_0 J^2$, etc. The order of each individual term is $\Omega + \Omega_v - 2$.

Such a Hamiltonian development scheme enables the treatment of any polyad system. In the present case, as described in Sec. III, we use the following effective Hamiltonians:

- The ground state effective Hamiltonian,

$$H^{(\text{GS})} = H_{\{\text{GS}\}}^{(\text{GS})}. \quad (4)$$

- The ν_i fundamental ($i = 30, 28, 27, 26$ or 23) effective Hamiltonian,

$$H^{(\nu_i)} = H_{\{\text{GS}\}}^{(\nu_i)} + H_{\{\nu_i\}}^{(\nu_i)}, \quad (5)$$

- The ν_{25}/ν_{24} dyad effective Hamiltonian,

$$H^{(\nu_{25}/\nu_{24})} = H_{\{\text{GS}\}}^{(\nu_{25}/\nu_{24})} + H_{\{\nu_{25}/\nu_{24}\}}^{(\nu_{25}/\nu_{24})}. \quad (6)$$

Correspondence between the parameters in Eq. (3) and other treatments (e.g., Robiette *et al.*³⁷) can be expressed

TABLE II. Spin statistical weights for adamantane $^{12}\text{C}_{10}\text{H}_{16}$.

Rovibrational symmetry species	A_1	A_2	E	F_1	F_2
Statistical weight	5536	5536	10944	16352	16352

(see Table IV below for the lowest orders). The present approach offers the advantage of being systematic and extendable up to any order of expansion and to any type of interacting polyad.

A dipole moment operator is developed in the same way (see for instance Champion *et al.*²⁷ for details about its construction). In the present work, where we do not precisely study absolute line intensities, it is expanded to zeroth order only for each of the analyzed bands.

We use here a vibrational basis restricted either to the ν_i ($i = 30, 28, 27, 26$ or 23) mode:

$$|\Psi_v^{(C_v)}\rangle = |\Psi_{\nu_i}^{(l_i, C_v)}\rangle, \quad (7)$$

or to the ν_{25} and ν_{24} modes coupled altogether:

$$|\Psi_v^{(C_v)}\rangle = |(\Psi_{\nu_{25}}^{(l_{25}, C_{25})} \otimes \Psi_{\nu_{24}}^{(l_{24}, C_{24})})^{(C_v)}\rangle, \quad (8)$$

i.e., we use harmonic oscillator wavefunctions for triply degenerate modes with vibrational angular momentum l_i . C_v is the overall vibrational symmetry species. The Hamiltonian and dipole moment matrix elements are calculated in the coupled rovibrational basis

$$|[\Psi_v^{(C_v)} \otimes \Psi_r^{(J, nC_r)}]^{(C)}\rangle, \quad (9)$$

$\Psi_r^{(J, nC_r)}$ being a rotational wavefunction with angular momentum J , rotational symmetry species C_r and multiplicity index n (see Champion *et al.*²⁷) and C the overall symmetry species ($C = C_v \otimes C_r$).

Line intensities also depend on the spin statistical weights, which can be calculated with the method of Berger³⁸ considering ten ^{12}C carbon atoms with zero nuclear spin and 16 hydrogen atoms with $1/2$ nuclear spin. The results are given in Table II.

III. RESULTS AND DISCUSSION

Adamantane has 11 triply degenerate IR active modes (F_2 symmetry) for which the calculated intensities range from 0.01 km mol^{-1} to 150 km mol^{-1} . In the experimental spectrum taken at low resolution (see Fig. 2), all IR active modes can be identified and in addition several hot bands and combination bands are observable. High-resolution scans of the individual vibrational modes revealing their rotational substructure are presented in the following. The ν_{29} IR active mode is so weak (calculated intensity of $0.005 \text{ km mol}^{-1}$) that no high resolution spectrum could be recorded for this mode using the present set-up. On the other hand, the three CH stretching modes ν_{20} , ν_{21} , and ν_{22} appear as broad unresolved saturated features. The high density of vibrational states, the presence of several hot bands, and the numerous possible anharmonic interactions prevented us from resolving the rotational structure in this part of the spectrum. Table III lists the frequencies of the vibrational band centers together with their assignment for the 11 IR active fundamental modes

FIG. 2. Low resolution IR spectrum of adamantane composed of two spectra recorded at different pressures of adamantane: the 600–4500 cm^{-1} part of the spectrum has been obtained at $P = 0.01$ mbar and the region 300–600 cm^{-1} has been recorded at $P = 0.1$ mbar. Propositions of assignment of the IR active fundamental modes and some combination bands are indicated. Lines of remaining H_2O are detected in the 1500 cm^{-1} and 3500 cm^{-1} regions.

and several combination bands, where several of the band positions listed are reported for the first time. The combination modes provide experimental values for effective anharmonic parameters of the IR modes involved.

In the following paragraphs we present the first rotational analysis and fit of 7 fundamental bands of adamantane: ν_{23} , ν_{24} , ν_{25} , ν_{26} , ν_{27} , ν_{28} , and ν_{30} . For the spectral analysis, it is possible to use the tools that have been developed previously for smaller tetrahedral molecules, importantly CH_4 . To this end, we make use of the STDS software,³⁹ which is now

TABLE III. Frequencies and assignments of the IR active fundamental modes as well as a proposition for several combination modes of adamantane.

Frequency / cm^{-1}	Assignment
442.371 ^a	ν_{30}
638.12 ^b	ν_{29}
797.622 ^a	ν_{28}
949.52 ^b	ν_{11}
969.591 ^a	ν_{27}
1101.998 ^a	ν_{26}
1315.154 ^a	ν_{25}
1357.443 ^a	ν_{24}
1455.918 ^a	ν_{23}
2671.9 ^b	$\nu_{24} + \nu_{25}$
2754.6 ^b	$\nu_{23} + \nu_{24}$
2858.9 ^b	ν_{22}
2911.9 ^b	ν_{21}
2937.6 ^b	ν_{20}
3354.7 ^b	$\nu_{21} + \nu_{30}$
3545.4 ^b	$\nu_{21} + \nu_{29}$
3953.8 ^b	$\nu_{22} + \nu_{26}$
4014.3 ^b	$\nu_{21} + \nu_{26}$
4172.5 ^b	$\nu_{22} + \nu_{25}$
4275.7 ^b	$\nu_{21} + \nu_{24}$
4352.0 ^b	$\nu_{21} + \nu_{23}$

^aIndicates the values obtained from the rotational analysis and fit.

^bIndicates values obtained from the maximum absorption.

part of XTDS.⁴⁰ This code is adapted to the vibrational modes of XY_4 tetrahedral molecules, so that it can be used for analyzing either a single F_2 fundamental band of adamantane by considering it as a “ ν_3 ” band of an XY_4 molecule, or two interacting F_2 fundamentals by considering it as a “ ν_3/ν_4 ” dyad of an XY_4 molecule. Although it would in principle be possible to consider more than two interacting bands, this would require a modification of the programs.

It should be noted that for fundamental bands of spherical top molecules, in the absence of strong perturbations, the selection rules are such that each upper state rovibrational level is reached by only one transition from the ground vibrational state. Therefore, combination differences cannot be determined so that it is impossible to simultaneously fit lower and upper state parameters. In the present case, we are thus forced to fix the ground state parameters. We do this by retaining only the zeroth order for the ground vibrational state, which leads to a single parameter, namely $t_{\{0\}\{0\}}^{(0,0,A_1)A_1A_1} = B_0$. Then, we compute a rough value for B_0 based on DFT calculations using the B3LYP density functional and the 6-31G(d,p) basis set as implemented in GAUSSIAN 03.⁴¹ B_0 was thus estimated at 1.6747 GHz (0.0558 cm^{-1}) and fixed to this value in the following.

To overcome this difficulty, it would be necessary to obtain ground state data in the microwave region. However, such a rotational spectrum, for a molecule with no dipole moment appears only due to centrifugal distortion effects and is thus extremely weak.⁴² Another possibility is to locate “forbidden” transitions arising from perturbations induced by interactions between bands. Such lines would allow one to compute ground state combination differences, but they are generally very weak too. The presence of many hot bands in the room temperature spectrum of $\text{C}_{10}\text{H}_{16}$ severely impedes the observation of such weak effects (centrifugal distortion spectrum or forbidden lines). A low-temperature spectrum would be very helpful here, if a sufficient signal to noise ratio can be reached. Such an experimental effort is beyond the scope of the present study.

The ground state of adamantane is a non-degenerate vibrational state of A_1 symmetry and the IR active modes lead to the 11 triply degenerate vibrational states of F_2 symmetry. For such degenerate states, Coriolis forces induced by rotation of the molecule lift the degeneracy causing a splitting into three components denoted as $F_2^{(+)}(J)$, $F_2^{(0)}(J)$, and $F_2^{(-)}(J)$. For the $F_2 - A_1$ transitions considered in this work, selection rules apply such that $F_2^{(-)}(J)$ states are reached in $\Delta J = +1$ transitions, $F_2^{(0)}(J)$ states in $\Delta J = 0$ transitions, and $F_2^{(+)}(J)$ states in $\Delta J = -1$ transitions. These selection rules thereby prevent the use of combination differences to deduce the ground-state rotational structure (see, e.g., Herzberg²⁶ for simple description of the rotational structure of spherical tops). Rotational levels possess A, E or F symmetries and the following selection rules apply: A – A, E – E, and F – F. When higher order rotation-vibration couplings are not considered, the A, E and F symmetries are degenerate, which gives for $F_2 - A_1$ transitions P- and R-branches consisting of single lines (the separation of two adjacent lines being slightly different in the P- and R-branches due to the first order Coriolis term). When second-order interactions become larger (Coriolis interactions

FIG. 3. High resolution spectra of the ν_{30} , ν_{28} , ν_{27} , ν_{26} , and ν_{23} bands. The upper trace (in blue) is the predicted spectrum and the lower trace (in red) is the experimental spectrum. The residuals expressed in 10^{-3} cm^{-1} are indicated at the bottom of the figure.

with one or several other vibrational states or centrifugal distortion effects), the energies of A , E and F levels split, which leads to the appearance of clusters of lines for every rotational transition in each of the branches.

In case of an F_2 vibrational mode, it has been demonstrated²⁶ that second-order Coriolis interactions occurring with other vibrational states having E or F_1 symmetry may cause a splitting of the A , E and F species. No

such splitting is expected for Coriolis interaction with singly-degenerate vibrational states as well as with F_2 states.

The 7 rotationally resolved IR active modes show relatively different rotational patterns. The experimentally determined transition frequencies were used to fit several molecular parameters of the Hamiltonian described in Sec. II B. As we show below, ν_{30} , ν_{28} , ν_{27} , ν_{26} , and ν_{23} can be treated as isolated bands. In contrast, ν_{25} and ν_{24} should be treated as

a dyad, with a strong Coriolis interaction between the two bands. Figure 3 shows the high resolution spectra of the ν_{30} , ν_{28} , ν_{27} , ν_{26} , ν_{23} bands and Fig. 8 shows the results for ν_{25} and ν_{24} . The upper traces (in blue) are the predicted spectra and the lower traces are the experimental spectra (in red). The residuals expressed in 10^{-3} cm^{-1} are indicated at the bottom of the figures. It should be noted that, because of the presence of several low-lying bending fundamental vibrational modes, our room temperature spectra exhibit many hot band lines. The present analysis is however restricted to the cold band lines. Nevertheless, hot band Q -branches are clearly visible adjacent to the Q -branch of a fundamental mode as one can see in Figs. 3 and 8.

In general, band analysis was performed as follows. First, the band-center $t_{\{i\}\{i\}}^{0(0,0A_1)} = \nu_i$ was fixed approximately to the position of the Q -branch head. Then, the upper state rotational constant $t_{\{i\}\{i\}}^{2(0,0A_1)} = B_i - B_0$ and the Coriolis constant $t_{\{i\}\{i\}}^{1(1,0F_1)} = 3\sqrt{2}(B\zeta)_i$ were varied by hand to get the correct spacing of the J clusters. Then, the $t_{\{i\}\{i\}}^{2(2,0E)}$ parameter was also varied to obtain the correct tetrahedral splitting within the J clusters. At this stage, it was possible to assign lines using the SPVIEW program.⁴⁰ Assignments in the very dense Q -branch regions were not always possible, depending on whether the structures are sufficiently resolved or not. When no Q -branch assignment was possible, the simultaneous fit of $t_{\{i\}\{i\}}^{2(2,0E)}$ and $t_{\{i\}\{i\}}^{2(2,0F_2)}$ was not possible (both parameters exhibit a 100% correlation when no Q -branch assignments are present in the fit); in that case, $t_{\{i\}\{i\}}^{2(2,0F_2)}$ was varied by hand and the other parameters were fitted again, until the Q -branch profile was correct.

A. ν_{30} centered at 442.4 cm^{-1}

Recording the weak ν_{30} absorption band (calculated intensity of about 0.1 km mol^{-1}) required the use of the bright synchrotron radiation as FIR continuum source in order to increase the signal to noise ratio. The rotational structure of the P - and R -branches are clearly visible in Fig. 4 and the splitting of the A , E , and F sublevels with the same J is observed for relatively low J values.

As already mentioned, second order interactions of rotational and vibrational motions are responsible for the splitting of the energy levels within a given J cluster. Centrifugal distortion as well as second-order Coriolis interaction with another vibrational mode of E or F_1 symmetry lying close in energy might be responsible for such a splitting. One may notice the proximity of the ν_{19} vibrational mode (F_1 symmetry) located at 355 cm^{-1} and more interestingly the ν_{12} mode (E symmetry) located at 400 cm^{-1} . Since these modes are IR inactive, experimental frequencies for these modes have been obtained by Raman spectroscopy of adamantane in condensed-phase samples.^{14,16} When strong Coriolis interaction occurs, the perturbing mode may become weakly active, but we did not detect any absorption in the region of ν_{12} or ν_{19} . Since no large perturbations were detected in the branches of ν_{30} , it was treated as an isolated band in the analysis. The intense Q -branch appears blue shaded (first spectrum of Fig. 3) and the rotational clusters of lines are partly resolved for high J values as shown in Fig. 4. In the largely unresolved Q -branch

FIG. 4. Zooms of two typical regions of the P - and R -branches of ν_{30} . Despite the relatively low signal to noise ratio, clusters of lines are well resolved for relatively low J values. As for Fig. 3 the predicted spectrum, the experimental spectrum and the residuals are indicated by blue, red and black traces.

structure, we clearly distinguish the presence of one or several other Q -branches belonging to hot bands. Since the spectra have been recorded at room temperature, the hot bands may involve several quanta of the low frequency modes centered at 355 cm^{-1} (ν_{19} mode, F_1 symmetry),¹⁶ 400 cm^{-1} (ν_{12} mode, E symmetry),¹⁴ and 442 cm^{-1} (ν_{30} mode, F_2 symmetry). The fit of the fundamental band included 3530 lines yielding 13 parameters of the Hamiltonian described in Sec. II B. As shown in Figs. 3 and 4, the calculated spectrum (blue traces) matches the experimental (red traces) very well in terms of positions; the RMS deviation is $0.49 \times 10^{-3} \text{ cm}^{-1}$, close to the expected experimental accuracy (a few times 10^{-4} cm^{-1} considering the signal to noise ratio of this part of the observed spectrum). The residuals are indicated at the bottom of each spectrum as black crosses, expressed in units of 10^{-3} cm^{-1} . Concerning the relative intensities of lines within a given cluster, the poor signal to noise ratio of the experimental spectrum as well as the presence of weaker lines belonging to hot bands lead to some discrepancies between the observed and calculated spectra.

B. ν_{29} centered at 638.1 cm^{-1}

The very weak ν_{29} mode (calculated intensity of about 0.01 km mol^{-1}) was detected for the first time. Due to

FIG. 5. Zooms of different regions of ν_{28} band. Clusters of lines are well resolved even for low rotational quantum numbers. Note the deviation of the predicted spectrum compared to the experimental for the clusters $R(29)$, $R(30)$ and $R(31)$, for which lines could not be assigned.

the poor signal to noise ratio of this band, no rotationally resolved spectrum could be obtained with our current experimental setup. We propose to assign the band center to the maximum of the absorption, which is located at 638.12 cm^{-1} .

C. ν_{28} centered at 797.6 cm^{-1}

As observed for the ν_{30} mode, the ν_{28} mode shows nicely resolved clusters of rotational lines in the P - and R -branches due to the splitting of the A , E and F term values of each rotational level. Figure 5 shows several regions of the ν_{28} band. The nearest vibrational levels which may cause Coriolis interaction with ν_{28} include ν_{18} (calculated at 887 cm^{-1} with F_1 symmetry)¹⁶ and ν_{11} (calculated at 917 cm^{-1} with E symmetry).¹⁶ Experimentally, the position of ν_{11} is known from Raman spectra:¹⁴ 953 cm^{-1} in solution and 950 cm^{-1} in a powder sample. In the next paragraph, we propose to assign to ν_{11} a band located at 949.42 cm^{-1} in our gas phase spectrum. Figure 5 shows the experimental spectrum of the ν_{28} mode together with the predicted spectrum and the residuals for the line positions. The calculation reproduces the experimental spectrum accurately both in terms of frequencies and intensities. The results of the fit are shown in Table IV: 7458 lines involving J values as high as 100 are included in the fit. Eleven parameters were necessary to fit the experimental data with an

RMS deviation of $0.32 \times 10^{-3} \text{ cm}^{-1}$. As for ν_{30} , ν_{28} has been treated as an isolated band despite the close presence of many other vibrational modes. A zoom of the R -branch covering transitions with $J = 78, 79$, and 80 is shown in Fig. 5. Note the small differences between the experimental and predicted spectra regarding the relative intensities of lines belonging to a given J value and having different symmetries. As for ν_{30} , signal to noise ratio and presence of hot band lines are suspected to cause these discrepancies. Figure 5 also shows a part of the P -branch involving $J = 62, 63, 64$. Many other lines involving hot bands are present between (and overlap) the assigned clusters of $P(62)$, $P(63)$ and $P(64)$. The hot bands may involve several quanta of the low-frequency modes centered at 355 cm^{-1} (F_1 symmetry), 400 cm^{-1} (E symmetry) and 442 cm^{-1} (F_2 symmetry).

In Fig. 5, one notices the larger discrepancies between experimental and predicted spectra for the $R(29)$, $R(30)$, and $R(31)$ line clusters. In the P -branch the corresponding lines do not appear to be affected by any perturbation, but a clear enhancement of their relative intensities is observed. This effect may be due to a local perturbation. The ν_5 mode located at 758 cm^{-1} having A_1 symmetry¹⁴ cannot be responsible for the splitting of the A , E , F species through Coriolis interaction, but might be responsible for a perturbation in the energy spacing (the F_2^- levels being more perturbed than the F_2^+). The reader is referred to Fig. 7 to get an impression of the

TABLE IV. Effective Hamiltonian parameters (see text for notations). Values are in cm^{-1} . Non-fitted parameters are fixed to zero. J_{max} is the maximum J value for assigned lines. Uncertainties in the last digits for each parameter are given in parentheses; they represent 1σ standard deviation obtained from the least-squares fit.

Parameter $\Omega(K, nC)$	ν_{30}	ν_{28}	ν_{27}	ν_{26}	ν_{25}	ν_{24}	ν_{23}	Notation from Robiette <i>et al.</i> ³⁷
0(0, 0A ₁)	442.371346(27)	797.622155(13)	969.590683(15)	1101.998660(16)	1315.154171(87)	1357.44334(16)	1455.917653(27)	ν_i
1(1, 0F ₁)	$-3.50150(11) \times 10^{-2}$	$-1.0749505(34) \times 10^{-1}$	$1.955644(67) \times 10^{-2}$	$2.855651(87) \times 10^{-2}$	$1.285199(63) \times 10^{-1}$	$3.2550(14) \times 10^{-2}$	$-2.298046(91) \times 10^{-2}$	$3\sqrt{2}(B\zeta)_i$
2(0, 0A ₁)	$3.3872(56) \times 10^{-5}$	$-4.81554(87) \times 10^{-5}$	$-2.6091(11) \times 10^{-5}$	$-6.0359(34) \times 10^{-5}$	-3.0×10^{-5} ^a	$-1.4053(48) \times 10^{-4}$	$1.8911(16) \times 10^{-5}$	$B_i - B_0$
2(2, 0E)	$-6.1258(84) \times 10^{-5}$	$3.1059(12) \times 10^{-5}$	$1.5646(26) \times 10^{-5}$	$3.6662(40) \times 10^{-5}$	$3.061(25) \times 10^{-5}$	$2.077(87) \times 10^{-5}$	$-1.3800(28) \times 10^{-5}$	$-(1/2)\alpha_{220}^i - 6\alpha_{224}^i$
2(2, 0F ₂)	$6.873(13) \times 10^{-5}$	$8.372(16) \times 10^{-6}$		$1.01112(58) \times 10^{-4}$	1.872×10^{-5} ^a			$-(3/4)\alpha_{220}^i + 6\alpha_{224}^i$
3(1, 0F ₁)	$-3.650(19) \times 10^{-8}$	$-6.709(21) \times 10^{-9}$	$1.4209(46) \times 10^{-8}$	$2.272(20) \times 10^{-8}$	$1.807(47) \times 10^{-6}$	$-1.728(49) \times 10^{-6}$	$-1.6930(60) \times 10^{-8}$	$-(3\sqrt{3}/4\sqrt{2})F_{110}^i$
3(3, 0F ₁)	$-2.735(14) \times 10^{-8}$	$7.530(15) \times 10^{-9}$	$-9.676(38) \times 10^{-9}$	$-3.9655(86) \times 10^{-8}$	$-4.221(76) \times 10^{-8}$	$3.926(85) \times 10^{-7}$	$-9.893(32) \times 10^{-9}$	$(3\sqrt{5}/2\sqrt{2})F_{134}^i$
4(0, 0A ₁)	$1.435(75) \times 10^{-9}$	$-1.43(15) \times 10^{-11}$	$9.07(57) \times 10^{-11}$	$5.70(24) \times 10^{-10}$	$7.32(72) \times 10^{-9}$	$5.28(83) \times 10^{-9}$	$-5.47(12) \times 10^{-11}$	$-(D_4 - D_0)$
4(2, 0E)	$1.123(92) \times 10^{-9}$	$-1.279(61) \times 10^{-11}$	$3.35(95) \times 10^{-11}$	$2.53(13) \times 10^{-10}$	$-4.38(18) \times 10^{-9}$	$1.64(78) \times 10^{-9}$		
4(2, 0F ₂)	$2.659(57) \times 10^{-9}$	$-3.5(2.3) \times 10^{-12}$		$7.87(25) \times 10^{-10}$	$-1.593(49) \times 10^{-9}$			
4(4, 0A ₁)	$-1.82(37) \times 10^{-11}$	$-1.99(42) \times 10^{-12}$	$1.17(25) \times 10^{-11}$	$-1.288(26) \times 10^{-10}$		$7.47(19) \times 10^{-9}$	$-1.082(51) \times 10^{-11}$	
4(4, 0E)	$-1.357(87) \times 10^{-10}$			$7.47(59) \times 10^{-11}$		$4.57(17) \times 10^{-9}$	$-5.00(11) \times 10^{-11}$	
4(4, 0F ₂)	$-2.22(68) \times 10^{-11}$			$-3.85(46) \times 10^{-11}$				
5(1, 0F ₁)				$-4.48(11) \times 10^{-13}$		$-9.52(27) \times 10^{-11}$		
5(3, 0F ₁)				$-1.89(41) \times 10^{-13}$		$2.171(66) \times 10^{-10}$		
5(5, 0F ₁)				$-7.77(49) \times 10^{-13}$		$1.002(82) \times 10^{-10}$		
5(5, 1F ₁)						$-2.97(12) \times 10^{-11}$		
6(0, 0A ₁)				$-1.430(38) \times 10^{-14}$				
1(1, F ₁)					$3.2550(14) \times 10^{-2}$			ν_{25}/ν_{24} Coriolis
2(0, 0A ₁)					$-1.4053(48) \times 10^{-4}$			ν_{25}/ν_{24} Coriolis
Lines fitted	3530	7458	2702	5798	846	1128	3 204	
J_{max}	95	100	100	107	80	56	100	
$d_{\text{RMS}}/10^{-3} \text{ cm}^{-1}$	0.49	0.32	0.34	0.25	0.77	3.16	0.50	

^aFixed value.

FIG. 6. Zoom on three clusters of the R -branch: $R(78)$, $R(79)$ and $R(80)$ of ν_{27} . Despite the smaller tetrahedral splitting of ν_{27} than ν_{30} and ν_{28} , the calculated spectrum fits well the experimental results. Many lines belonging to a relatively intense hot band centered at 970.2 cm^{-1} are observed between the three clusters of lines belonging to the fundamental transition.

energy spacing between F_2^- , F_2^0 , F_2^+ as well as the much smaller A, E, F splitting. The Q -branch of this mode shows largely unresolved red shading. Presence of hot band Q -branches may explain the discrepancy in the width of the calculated vs. experimental spectra.

D. ν_{27} centered at 969.5 cm^{-1}

The ν_{27} mode also shows clear rotational structure in the P - and R -branches, whereas the Q -branch is an intense unresolved feature. The splitting of the A, E, and F species clearly observed in the clusters of lines for the ν_{30} and ν_{28} modes is small for the ν_{27} mode shown in Fig. 6. Even for high J values (where large centrifugal distortion effects are expected), the splitting of the rotational levels remains relatively small. The rovibrational transitions appear as sharp single lines for low J values evolving to broader lines for higher rotational quantum numbers. Nevertheless, some weak splitting has been identified and we assigned 2702 lines for this band. 9 parameters have been fitted to with an RMS deviation of $0.34 \times 10^{-3}\text{ cm}^{-1}$.

In the Q -branch region, one notices broad Q -branches assigned to hot bands involving one or several quanta of the lowest vibrational levels (see Fig. 3). In particular a hot band located at 970.2 cm^{-1} shows relatively intense transitions observed between the lines belonging to the the P - and R -branches of ν_{27} (see the unassigned lines observed between the three clusters of lines belonging to the fundamental transition in Fig. 6). These lines exhibit a clear A, E, F splitting for the transitions involving high J levels. The analysis of this band has not been further pursued here and will be the subject of further studies.

Interestingly, another band belonging to adamantane has been located at 949.52 cm^{-1} (for the maximum absorption). It shows very clear rotational structure with a relatively large tetrahedral splitting in the P - and R -branches. We propose to assign this band to the IR inactive ν_{11} of E symmetry, which has been observed experimentally by Raman spectroscopy at

953 cm^{-1} in solution and at 950 cm^{-1} in a powder sample.¹⁴ The observation of this mode in the present IR spectrum must be due to an intense interaction with an IR active mode which has to result in a large splitting of the A, E, F species. The ν_{27} mode at 969.5 cm^{-1} does not appear to be affected by this mode since it shows only relatively weak splitting, while ν_{28} (797.6 cm^{-1}) and ν_{26} (1101.8 cm^{-1}) show large splitting of their rotational levels.

E. ν_{26} centered at 1102 cm^{-1}

As predicted by the DFT calculations, the ν_{26} mode located at 1102 cm^{-1} is about 10 times more intense than the ν_{28} mode, so that its Q -branch is saturated in the experimental spectrum. As for ν_{28} , the clusters of lines are fully resolved for relatively low J values in the P -branch (see Fig. 7). The splitting is so large that lines involving different J values overlap for high rotational quantum numbers. Several vibrational modes may be good candidates for Coriolis interaction with ν_{26} , in particular the ν_{11} (E symmetry and proposed to be centered at 949.52 cm^{-1} in the gas-phase spectrum) and ν_{16} (F_1 symmetry and calculated at 1098 cm^{-1} by Jensen¹⁶) modes. Significant Coriolis interaction with ν_{11} is possible and a weak absorption located at 1110.4 cm^{-1} is observable, which may be assigned to ν_{16} becoming weakly IR active through Coriolis interaction. Despite these possible interacting states, large perturbations in the positions and intensities of the clusters of rotational transitions are not observed, so that as for the bands discussed above, excitation of the ν_{26} mode has been treated as an isolated band. As shown in Fig. 7, the Q -branch appears to be sufficiently well resolved to perform rotational assignments; the calculated spectrum matches the experimental results well. Figure 7 shows the reduced energies plotted against J to show the relatively strong first-order Coriolis interaction splitting the levels in F_2^+ , F_2^0 , and F_2^- sub-levels and the finer effects leading to the detection of clusters of lines for a given J .

For ν_{26} , 5798 lines were included in the fit of 17 parameters, higher order parameters were necessary to fit lines involving J values as high as 107. The results of the fit are shown in Table IV and a typical part of this band system is shown together with the simulation in Fig. 7. The simulated spectrum matches the experimental results both in frequency and intensity.

F. ν_{25} centered at 1315.0 cm^{-1} and ν_{24} centered at 1357.3 cm^{-1}

Figure 8 shows the experimental and calculated spectra of ν_{25} and ν_{24} vibrational modes. The ν_{25} mode is a relatively weak mode at 1315.0 cm^{-1} for which the band shape is rather different from all other bands discussed above. The Q -branch shows a very sharp cut off on the low J edge, it is red-shaded and many lines appear fully resolved. The P -branch shows an irregular intensity distribution for high J values indicative of possible perturbations with another vibrational state. The clusters of lines in the P - and R -branches are partly resolved for high J levels.

FIG. 7. Zoom of typical regions of the P -, Q -, and R -branches of ν_{26} showing well resolved clusters of lines. In contrast with the other bands, the Q -branch is well resolved and allowed to perform rotational assignments. Reduced energies (given in cm^{-1}) are plotted against J to show the relatively strong first order Coriolis interaction and the finer effects leading to the formation of clusters of lines for a given J .

The appearance of the ν_{24} mode is similar to those of ν_{30} , ν_{28} and ν_{26} . The Q -branch is broad and unresolved, while the P - and R -branches show a large tetrahedral splitting even for transitions involving relatively low J levels. A notable

enhancement of the intensities of several low- J lines in the R -branch is also noted.

In this spectral region, many levels may affect ν_{25} and ν_{24} through perturbations. The ν_{14} and ν_{15} modes (F_1 symmetry) observed at 1321 cm^{-1} and 1288 cm^{-1} , respectively, in the IR spectrum of phase transition crystalline adamantane¹⁴ as well as ν_9 (E symmetry)¹⁴ at 1370 cm^{-1} may cause perturbations in the ν_{25} and ν_{24} manifolds. In addition, many combination modes are present in this spectral region which may also be responsible for the perturbations. We note a weak absorption feature located at about 1325 cm^{-1} , which we assign to the weak $2\nu_{29}$ overtone.

The main perturbation, however, is likely a Coriolis interaction between ν_{25} and ν_{24} themselves. Therefore, we treat these bands as an interacting dyad (by considering them as a “ ν_3/ν_4 ” dyad of an XY_4 molecule, as explained above). As shown in Table IV, a satisfactory fit is obtained, giving values for two Coriolis interaction parameters. In total, 848 and 1128 lines were assigned in the ν_{25} and ν_{24} bands, respectively. This allows in particular to reproduce the unusual P -branch intensity pattern of ν_{25} , as is shown in Fig. 8. One should notice the intense absorption lines from residual water marked by a star in Fig. 8. Also, as for the other modes studied in this work, large discrepancies due to the presence of hot bands are

FIG. 8. Experimental and simulated spectra of the ν_{25}/ν_{24} dyad. The well-reproduced intensity pattern in the ν_{25} P -branch should be noticed. A strong discrepancy between observed and calculated line positions appears at $J = 33$ in the ν_{24} R -branch. Intense sharp lines (marked by a star) are due to water absorption.

FIG. 9. Typical parts of the P - and R -branches of the intense ν_{23} mode. Tetrahedral splittings are observed only for high values of J .

observed between the experimental and calculated spectra in the Q -branch region. It appears, however, that the ν_{24} band remains difficult to fit correctly. Rotational lines in this band were assigned up to $J = 56$ only, with strong perturbations appearing in the R -branch at $J = 33$. The intensity pattern for this mode might also be affected by the perturbations which were not accounted for. Resolving this issue would require further investigations to identify the perturbing state(s).

G. ν_{23} centered at 1455.9 cm^{-1}

The ν_{23} fundamental band has high intensity, so that the experimental spectrum has been recorded at a reduced pressure of $P = 0.01 \text{ mbar}$ (see Table I). The Q -branch is unresolved and many hot bands (and possibly combination modes) are present, which blur the experimental spectrum. Figure 9 shows the weak tetrahedral splittings in P - and R -branches observed for relatively high J values ($J \geq 80$), although they are less pronounced than for example the ν_{28} mode. As for ν_{24} and ν_{25} many vibrational levels may be in Coriolis interaction with ν_{23} . Despite the presence of neighboring possibly perturbing states, we treated the ν_{23} band system as isolated since no large perturbations were noticed. The fit of in total 3204 lines resulted in the determination of 9 Hamiltonian

parameters. The accuracy of the fit is indicated by an RMS deviation of $0.50 \times 10^{-3} \text{ cm}^{-1}$. The presence of hot band lines leads to relatively large baseline variations, which causes irregular intensity patterns not reproduced in the calculations.

In the spectrum recorded at $P = 0.1 \text{ mbar}$ we identified the $\nu_{27} + \nu_{30}$ combination band at about 1411.2 cm^{-1} , slightly red-shifted by anharmonic effects. This band also shows large tetrahedral splitting in the P - and R -branches. Analysis of this band will be subject of further study.

IV. CONCLUSION AND PERSPECTIVES

We presented the first rotationally resolved IR spectra of adamantane, recorded via long-pathlength FTIR spectroscopy making use of synchrotron radiation as a source for bright broadband FIR radiation. We were able to resolve the rotational structure of 7 out of 11 IR active fundamental bands. Several combination modes were observed for the first time in the gas-phase as well, which could partially be resolved rotationally. In these high-resolution spectra, several bands show clusters of rotational lines typical of spherical top molecules, induced by the splitting of each rotational J level into sub-levels of A , E , and F species. These splittings originate in rotation-vibration interactions, such as Coriolis interactions with vibrational modes of E or F_1 symmetry, as well as in centrifugal distortion effects. The rotationally resolved band systems were analyzed using a Hamiltonian that was previously used to analyze XY_4 tetrahedral species. The fitting of thousands of transitions to this Hamiltonian resulted in an accurate determination of various spectroscopic parameters of adamantane, which may for instance aid in the identification of adamantane in the interstellar medium. To date, very few astrophysical sources show features assigned to diamond-like materials in the $3 \mu\text{m}$ spectral region.⁷ The most prominent sources reported to date are the two Herbig stars HD97048 and Elias 1, where the $3.43 \mu\text{m}$ and $3.53 \mu\text{m}$ features were tentatively assigned to the intense CH stretching modes of hydrogen terminated crystalline facets of relatively large diamond nanocrystals.⁶ These two sources and more generally carbon rich Asymptotic Giant Branch (AGB) stars where a large variety of carbon bearing molecules (Polycyclic Aromatic Hydrocarbons,⁴³ fullerenes,⁴⁴ polyynes, cyanopolyynes,⁴⁵ ...) have been identified might be good candidates to search for adamantane signatures. Adamantane may also be searched for in C-rich circumstellar envelopes, such as IRC+10216 or CRL618 where many small hydrocarbon molecules have already been identified.^{46,47}

Our work reports accurate transitions for 7 of the 11 IR active modes of adamantane but the three most intense bands are the CH stretching modes which could not be resolved in our work. To circumvent this problem, an experiment making use of the Jet-AILES apparatus is planned to record the jet-cooled absorption spectrum in the $3 \mu\text{m}$ region (see Cirtog *et al.*⁴⁸ for a description of the Jet-AILES apparatus), which might be more appropriate for a potential detection in space using for example the high spectral resolution instruments available at the Very Large Telescope (see, e.g., CRIRES (Ref. 49) and VISIR (Ref. 50) spectrometers),

the instruments available at GEMINI or KECK observatories, or in the spectra already recorded by the Short Wavelength Spectrometer instrument onboard the ISO satellite. Also adamantane exhibits weak pure rotational spectra within its lowest vibrational modes. Very recently, in a collaboration with L. Margulès and R. Motiyenko at the PhLAM laboratory (France), we recorded and analyzed data in the 60–300 GHz spectral region (to be published). This future work might increase the chances for a radioastronomical detection of adamantane.

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