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Free-jet absorption millimeter-wave spectrum of 2'-aminoacetophenone

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ABSTRACT

The rotational spectrum of 2'-aminoacetophenone has been recorded and assigned using a Stark-modulated Free-Jet Absorption Millimeter-Wave (FJ-AMMW) spectrometer in the 59.6–74.4 GHz frequency range. Some transition lines show a hyperfine structure due to the internal rotation of the methyl group. A global fitting including previous measurements performed in the microwave region allowed the determination of the D_J and D_K quartic centrifugal distortion constants and methyl internal rotation barrier V_3 = 644(3) cm^{-1} value. The A–E tunnelling splitting is estimated to be Δ_0 = 23 MHz. Calculations at the MP2/aug-cc-pVTZ level underestimate the height of the V_3 barrier by about 23 cm^{-1}. This difference increases to 150 cm^{-1} with B3LYP-D3(BJ)/Def2-TZVP.

1. Introduction

Aminoacetophenones are a family of disubstituted aromatic compounds including three isomers, according to the position of the amino group with respect to the acetyl: 2'-aminoacetophenone (2AA), 3'-aminoacetophenone (3AA) and 4'-aminoacetophenone (4AA), as shown in Fig. 1. A comparative study of their properties can help in understanding the through-bond and through-distance effects taking place in molecules. For this reason, the rotational spectra of the three aminoacetophenone isomers have been recently investigated by rotational spectroscopy [1,2]. It has been demonstrated that the amino group is non-planar in 3AA and 4AA [2], whereas due to the formation of an intramolecular hydrogen bond with the oxygen atom, the amino group in 2AA is planar [1]. In the case of 3AA and 4AA both the 2–8 GHz and 59.6–74.4 GHz spectral regions were investigated, through chirped pulse molecular beam Fourier transform microwave (CP-MB-FTMW) spectroscopy and free-jet absorption Stark-modulated millimeter-wave (FJ-AMMW) spectroscopy, respectively. The combined results allowed the disentangling of the hyperfine structure due to both ^{14}N-nuclear quadrupole coupling (NQC) and the methyl internal rotation [2]. Differently, for 2AA only low-frequency measurements with CP-MB-FTMW have been reported up to now. This spectrum is characterized by the ^{14}N-NQC hyperfine structure, while there is no evidence of splitting due to methyl internal rotation [1]. However, to understand how the proximity of the substituents affects the methyl internal rotation barrier, it would be interesting to determine its value. Since the tunnelling splitting is expected to increase at higher frequencies, we decided to extend the study of 2AA in the 59.6–74.4 GHz range where some split lines can be resolved.

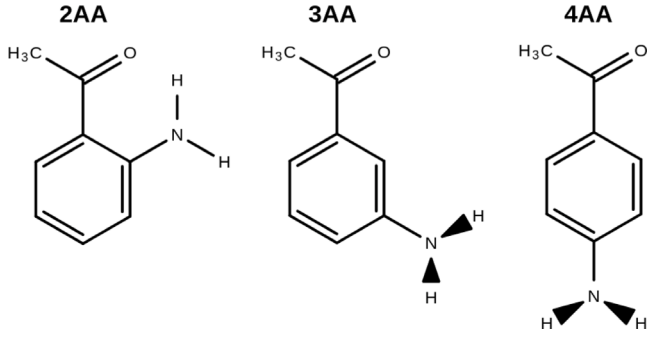

Fig. 1. Sketch of the 3 isomers of aminoacetophenone.

2. Experimental methods

The millimeter-wave spectrum was recorded in the 59.6–74.4 GHz frequency region by a Stark modulated FJ-AMMW spectrometer which

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has been described in previous works [3,4]. A synthesizer with a frequency range 0.002–40 GHz is utilized as the radiation source. The radiation from the source is fed into a ×4 multiplier chain composed of two doublers. The first one is active and includes the amplification of the generated harmonic frequency while the second is passive and the output power of the generated frequency is quite low (output power −3 to 0 dBm). The existence of the isolator improves the coupling between neighbouring members of the chain, while the filter between the two multipliers eliminates any undesirable harmonic signals. A Schottky diode detector in combination with a lock-in amplifier using the Stark modulation frequency as a reference, is employed to detect the transmitted power. The supersonic jet is generated from the expansion of argon gas ($P_0 \simeq 20$ kPa) to a backing pressure $P_b = 0.5$ Pa through a 0.3 mm pinhole nozzle. The millimeter-wave radiation and the free-jet are arranged perpendicularly, and a high voltage Stark modulation (electric field up to 750 V cm^{-1} at a frequency of 33 kHz) is applied to the molecular sample. After detection, the modulated signal is fed to a lock-in amplifier. The spectrometer is computer-controlled via a National Instrument GPIB board that communicates with the HP synthesizer in order to guide the frequency scan step by step and with the lock-in amplifier. The signal provided by the Schottky diode detector is recovered, amplified, and then collected according to the chosen gate time. The accuracy of the frequency measurements is better than 50 kHz and a resolution of 300 kHz can be achieved. The rotational temperature is estimated to be around 10 K. A commercial sample of 2AA (C_8H_9NO, CAS no. 551-93-9, purity 98%, b.p. 526–528 K, m.p. 293 K) was used without further purification. The sample was heated at $T = 383$ K, using a stagnation pressure $P_0 = 12$ kPa (120 mbar).

Table 1
Measured frequencies (ν) and fitted deviations ($c - o$) of the rotational transition lines of 2'-aminoacetophenone.

$J''(K_a'', K_c'') - J'(K_a', K_c')$		ν/MHz	$c - o$/MHz
14(14,1)–13(13,1)	E	61 333.35	0.01
14(14)–13(13)[a]	A	61 333.62	0.03
15(13,3)–14(12,3)	E	60 917.39	0.02
15(13)–14(12)	A	60 917.64	0.02
15(15)–14(14)	A	65 801.49	−0.01
16(12)–15(11)	A	60 489.68	0.00
16(13)–15(12)	A	62 940.79	0.05
16(14)–15(13)	A	65 385.93	0.01
16(15)–15(14)	A	67 828.22	−0.03
16(16,1)–15(15,1)	E	70 269.06	−0.03
16(16)–15(15)	A	70 269.33	−0.02
17(12)–16(11)	A	62 502.20	−0.01
17(13,5)–16(12,5)	E	64 960.23	−0.03
17(13)–16(12)	A	64 960.52	0.01
17(14)–16(13)	A	67 409.68	0.01
17(15)–16(14)	A	69 854.09	0.00
17(16)–16(15)	A	72 296.13	−0.01
18(13,6)–17(12,6)	E	66 975.37	−0.01
18(13)–17(12)	A	66 975.68	0.04
18(14)–17(13)	A	69 430.58	−0.03
18(15)–17(14)	A	71 878.34	0.03
19(12,8)–18(11,7)	A	66 502.02	0.08
19(12,7)–18(11,8)	A	66 502.24	−0.20
19(13,7)–18(12,7)	E	68 984.38	0.02
19(13)–18(12)	A	68 984.64	0.02
19(14)–18(13)	A	71 447.68	−0.01
19(15,5)–18(14,5)	E	73 899.91	0.02
19(15)–18(14)	A	73 900.14	−0.02

[a] μ_b-type asymmetry degenerate transition lines, only the K_a values are reported.

3. Computational methods

Geometry optimization and harmonic vibrational frequency calculations were performed with the Gaussian16® software package (G16, Rev. A.03)[1] using both the *ab initio* and density functional theory (DFT) approaches. As regards DFT, the Becke-three-parameters Lee–Yang–Parr hybrid functional (B3LYP [5,6]) was used corrected with the D3 version of Grimme's dispersion with Becke–Johnson damping (D3(BJ) [7]). *Ab initio* calculations were performed through the Møller-Plesset second-order perturbation theory (MP2 [8,9]). In both cases, a valence triple-ζ quality basis set was used: Karlsruhe polarized Def2-TZVP [10] for DFT and Dunning correlation consistent polarized augmented with diffuse functions type aug-cc-pVTZ [11] for MP2. The Gaussian input and output files for both 2AA and the parent species acetophenone can be found in the AMS Acta repository [12].

4. Results

The rotational spectrum of 2AA and its isotopologues was first assigned in the 2–8 GHz frequency range. Both μ_a and μ_b-type transition lines were observed and, in agreement with the determined spectroscopic constants, 2AA shows a C_s structure characterized by a hydrogen bond between the carbonyl and the amino groups [1]. According to these results, the rotational spectrum of 2AA has been predicted in the 59.6–74.4 GHz spectral region. Several weak $R - \mu_b$-type rotational transition lines were detected with J'' ranging from $J'' = 14$ to $J'' = 19$ and the $K_a\varepsilon$ values ranging from $K_a'' = 12$ to $K_a'' = 16$ (Table 1). No splitting due to the ^{14}N-NQC could be resolved, but seven transitions show a small A/E splitting (0.2–0.3 MHz) where the E-component apparently follows the μ_c-type selection rule (Fig. 2).

The overall set of detected lines was analysed using the combined axis method (CAM [13]) implemented in the XIAM program [14], which fits a set of spectroscopic constants common to both the A and E states and directly supplies the methyl internal rotation barrier. The Hamiltonian for a one-top problem can be written as:

$$H = H_R + H_{CD} + H_{NQC} + D^{-1} \times H_i \times D \quad (1)$$

where single rigid rotor H_R, centrifugal distortion H_{CD} and ^{14}N-NQC H_{NQC} operators are treated in the principal axis system (PAS) and used for both the A and E states, while the internal rotation Hamiltonian H_i is set up in the rho-axis system (RAM) and then rotated into the PAS using a rotation matrix D. As regards the internal rotation parameters, the barrier of a three-fold potential (V_3) was freely optimized during the fitting procedure while the values of geometrical parameters such as the reduced internal rotation constant (F_0) and the angles between the internal rotor axis (i) and the principal axes of inertia were fixed to those of the MP2/aug-cc-pVTZ calculated structure. In particular, assuming that the methyl internal rotation axis (i) matches the C–CH$_3$ bond, the (i, c) angle was fixed to 90°, while the (i, a) angle was fixed to the value of the angle between the C–CH$_3$ bond and the a axis. The S-reduction in I^r-representation was used in the fit and different uncertainties were applied to CP-MB-FTMW (15 kHz) and FJ-AMMW (50 kHz) data. The input and output files for the XIAM code are freely available at the AMS Acta repository [12], while the obtained spectroscopic constants are listed in Table 2 with the theoretical values. The standard deviation of the fit is given by the average error between the lines acquired with the CP-MB-FTMW and the ones acquired with the FJ-AMMW instrument; the standard deviation obtained fitting only the lines in the millimeter frequency range is 0.05 MHz.

5. Discussion

The agreement between the fitted and predicted values of the D_J and D_K quartic centrifugal distortion constants is acceptable (Table 2). The experimental data obtained for 3AA ($D_J = 0.020(1)$ and $D_K = 0.201(3)$ kHz) and 4AA ($D_J = 0.0120(5)$ and $D_K = 0.358(5)$ kHz) have the same order of magnitude [2], suggesting that the experimental data are reliable.

[1] Gaussian is a registered trademark of Gaussian, Inc. 340 Quinnipiac St. Bldg. 40 Wallingford, CT 06492 USA.

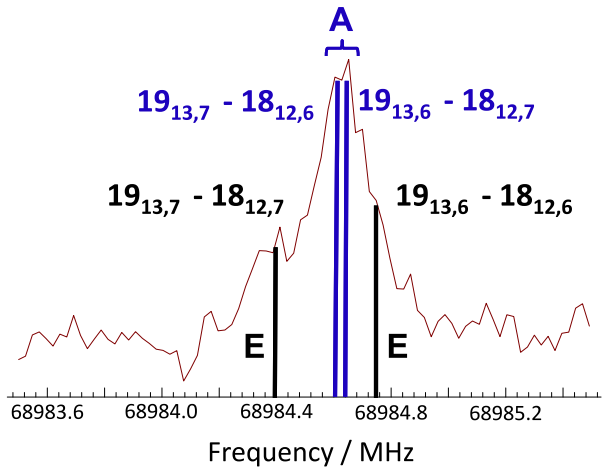

Fig. 2. Portion of the recorded spectrum of 2'-aminoacetophenone showing the $19_{13} \leftarrow 18_{12}$ transition lines. The most intense peaks correspond to the μ_b A-type transitions; the outer peaks are the forbidden μ_c E-type lines.

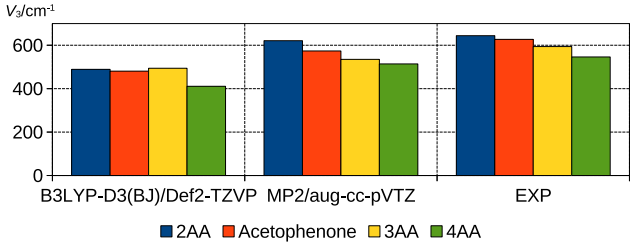

Fig. 3. Comparison of the theoretical and experimental methyl internal rotation barrier values of acetophenone and its amino derivatives (2AA, 3AA and 4AA).

Table 2
Experimental and theoretical spectroscopic parameters of 2'-aminoacetophenone in the *S*-reduction and I^r representation.

Parameter[a]	DFT[b]	MP2[c]	XIAM[d]
A /MHz	2249.986	2236.526	2234.1315(3)[e]
B /MHz	1211.727	1213.358	1204.7090(2)
C /MHz	791.433	790.857	787.0675(1)
D_J /kHz	0.026	0.024	0.0356(4)
D_{JK} /kHz	0.030	0.013	–
D_K /kHz	0.115	0.105	0.1192(8)
χ_{aa} /MHz	1.357	1.161	1.195(3)
χ_{bb}-χ_{cc} /MHz	6.957	6.334	6.406(5)
V_3 /cm^{-1}	489	621	644(3)
N	–	–	159
σ /MHz	–	–	0.020
μ_a /D	1.74	1.54	
μ_b /D	0.35	0.70	
μ_c /D	0.	0.43	
Δ_0 /MHz	119	29	23

[a] A, B, and C are the rotational constants. D_J, D_{JK}, D_K are quartic centrifugal distortion constants. χ_{gg} ($g = a$, b or c) are ^{14}N nuclear quadrupole coupling constants. V_3 is the methyl internal rotation barrier. N is the number of transition lines fitted, including 28 newly measured lines and all the previously assigned lines [1]. σ is the standard deviation of the fit. μ_g ($g = a$, b or c) are the electric dipole moment components. $\Delta_0 = E_E - E_A$ is the methyl internal rotation tunnelling splitting.

[b] B3LYP-D3(BJ)/Def2-TZVP.

[c] MP2/aug-cc-pVTZ.

[d] Structural parameters in the fit are fixed to the MP2/aug-cc-pVTZ values: F_0=161.63 GHz, $\widehat{i,a} = 60°$, $\widehat{i,c} = 90°$ (see text for details).

[e] Error in the unit of the last digit.

As regards the methyl internal rotation potential energy barrier, a threefold path with an experimental barrier V_3 = 644(3) cm^{-1} has been found. This value is bigger than those determined for the other aminoacetophenone isomers, the barrier being V_3 = 594(1) cm^{-1} for 3AA and V_3 = 545.7(5) cm^{-1} for 4AA [2]. It better compares to the value of the parent compound acetophenone V_3 = 627(3) cm^{-1} [15].

Both DFT and *ab-initio* calculations underestimate this value. However, the discrepancy is one order of magnitude lower at the MP2/aug-cc-pVTZ level of calculation (23 cm^{-1}) than B3LYP-B3(DJ)/Def2-TZVP (150 cm^{-1}). An extended comparison, including acetophenone (V_3(DFT) = 481, V_3(MP2) = 574 cm^{-1}), 3AA and 4AA is given in Fig. 3. It confirms that the *ab initio* results are closer than the DFT ones to the experimental values and also the trend among different molecules is better reproduced. A threefold potential energy surface leads to a barrier-dependant tunnelling splitting of the vibrational levels into a non-degenerate A-level and two degenerate E-levels. The tunnelling splitting for the vibrational ground state can be estimated as:

$$\Delta_0 = E_E - E_A = \frac{27}{8} \cdot F \cdot w_1^{v=0} \quad (2)$$

where F is the reduced rotational constant for internal rotation and $w_1^{v=0}$ is the Fourier coefficient of Mathieu eigenvalues for the ground state associated with the reduced barrier s [16]. In the present case, using F = 163105 MHz, s = 52.6, and $w_1^{v=0} = 4.18 \cdot 10^{-5}$, the estimated tunnelling splitting is 23 MHz.

6. Conclusions

In this work, previous rotational spectroscopy measurements of 2AA performed in the 2–8 GHz microwave region were extended to the 59.6–74.4 GHz spectral region. Despite the small value of the μ_b electric dipole moment component, 28 transition lines could be observed. Among them, 7 E-type μ_c-forbidden transition lines related to the methyl internal rotation tunnelling splitting were identified. A global fit performed with XIAM allowed the determination of two quartic centrifugal distortion constants and the methyl internal rotation barrier, that is higher than those of acetophenone, 3AA and 4AA. Comparison with simulated data probed that MP2/aug-cc-pVTZ calculations are better than B3LYP-B3(DJ)/Def2-TZVP calculations in reproducing both the absolute V_3 values and the trend among different molecules.

CRediT authorship contribution statement

Salvatore Boi: Writing – review & editing, Investigation, Formal analysis. **Sonia Melandri:** Writing – review & editing, Supervision, Formal analysis. **Luca Evangelisti:** Writing – review & editing, Supervision, Formal analysis. **Assimo Maris:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data supporting the findings of this study are openly available in the University of Bologna repository at http://dx.doi.org/10.6092/unibo/amsacta/7977.

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