



## Ring puckering splitting and structure of indan



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### ABSTRACT

The ground state ring puckering splitting of the cyclopentane ring of indan has been precisely determined ( $\Delta E_{01} = 22.364(1)$  MHz) by measuring the very weak  $\mu_c$ -type transitions with pulse jet Fourier transform microwave spectroscopy. In addition, the rotational spectra of all  $^{13}\text{C}$  monosubstituted isotopologues have been assigned and measured in natural abundance, leading to an accurate structure of the heavy atoms frame.

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### 1. Introduction

Molecules formed by the condensation of a six-membered aromatic ring and a five-membered saturated ring are characterized by three large amplitude motions: ring puckering, flapping and ring twisting. Information on these large amplitude motions have been obtained by microwave (MW), far infrared (FIR), vibrationally or rotationally resolved laser induced fluorescence (LIF) and from a combination of these techniques for a variety of this class of condensed-ring compounds [1–18]. It has been shown in several cases that an unambiguous determination of the barrier to ring puckering can be obtained only when the MW measurements of the ring puckering tunneling splitting in the ground state are available [3,4,6,10,15].

Indan can be considered as the prototype model for this kind of molecular systems. Five spectroscopic investigations are reported in the literature, related to the above mentioned large amplitude motions [1–3,18–20]. They concern the following techniques: FIR [1], vibronic [2,18], MW [3], one-color, resonance enhanced two-photon ionization spectra (R2PI) and dispersed fluorescence (DF) [19], and two-color resonantly enhanced multiphoton ionization and zero-kinetic-energy photoelectron spectroscopy [20], respectively.

The rotational spectrum of indan has been reported a long time ago, measured with conventional MW spectroscopy [3]. Due to the very low value of the  $\mu_c$  dipole moment component, it was not possible to measure the interstate  $\mu_c$ -type transitions, which supply

directly the value of the vibrational tunneling splitting. This splitting was indirectly estimated by MW-RF double resonance experiments, observing the intensity change of some rotational transitions while changing the value of a radiofrequency signal applied to the Stark electrodes. Nowadays, it is feasible, with pulsed Fourier transform MW spectroscopy, to measure even quite weak transitions. For this reason, we decided to measure the  $\mu_c$ -type transitions of the most abundant isotopic species (normal) of indan, and in order to determine the molecular structure, the rotational spectra of its  $^{13}\text{C}$ -mono substituted isotopologues in natural abundance. The molecular shape of indan, inclusive of the principal axes and of the atom numbering used through the text, is shown in Fig. 1.

### 2. Experimental methods

A commercial sample of indan 98% (Aldrich) was used without further purification. The spectra of the mono-substituted  $^{13}\text{C}$  isotopologues were analyzed in natural abundance.

The rotational spectra have been measured with pulsed jet Fourier-transform microwave (FT-MW) spectroscopy [21], in a coaxially oriented beam-resonator arrangement-(COBRA)-type [22]. The spectrometer, working in the 6–18.5 GHz frequency region, is described elsewhere [23]. Helium, as carrier gas, was passed over indan at 60 °C temperature, at a backing pressure of about 0.2 MPa, and expanded through the pulsed valve (General valve, series 9, nozzle diameter 0.5 mm) into the Fabry–Perot cavity to about  $1 \cdot 10^{-3}$  Pa. The spectral line position was determined after Fourier transformation of the 8 k data point time domain signal, recorded at intervals of 100 ns. Each rotational transition is

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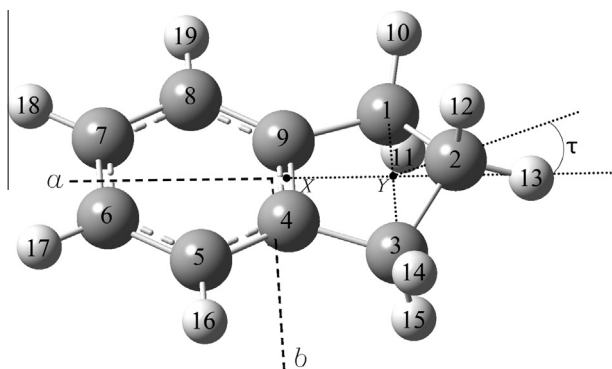


Fig. 1. Molecular shape, principal axes and atom numbering of indan.

split by Doppler effect, enhanced by the coaxial arrangement of the supersonic jet and resonator axes in the COBRA-FTMW spectrometer. The rest frequency is calculated as the arithmetic mean of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz and lines separated by more than 7 kHz are resolvable.

### 3. Results and discussion

#### 3.1. Rotational spectra

The  $\mu_a$ -spectrum of the most abundant species has been easily identified, based on the rotational constants determined in the previous absorption room temperature MW investigation [3]. Although being intrastate transitions, they displayed small splittings, due to the difference of the rotational constants of the two tunneling states originated by the above mentioned ring puckering motion. To detect the much weaker  $\mu_c$ -type lines we needed the maximum MW pulse power of the spectrometer and to warm up the sample to 60 °C before of the supersonic expansion, in order to increase its concentration in the beam. All these interstate transitions were split into two evenly separated (by ca 44.7 MHz, the double of the ring puckering splitting) component lines. We have been able to measure 67  $\mu_a$ -type and 14  $\mu_c$ -type transitions, which have been fitted together with the rotational frequency reported in Ref. [3]. In the fit, the appropriate weight was given to the two sets of measurements.

All transitions have been fitted simultaneously with a coupled Hamiltonian using the Pickett set of programs [24]. We used the following expressions:

$$H = \sum_i H_i^R + H^{CD} + \Delta E_{01}, \text{ with } i = 0, 1 \quad (1)$$

where  $H_i^R$  represents the rotational Hamiltonian for the state  $i$ .  $H^{CD}$  accounts for the centrifugal distortion corrections, corresponding to the  $I'$ -representation of Watson's "S" reduced Hamiltonian [25], assumed to be the same for both states.  $\Delta E_{01}$  is the energy difference between the  $\nu = 0$  and  $\nu = 1$  tunneling states. The spectroscopic constants obtained are reported in Table 1.

A general improvement on the uncertainties of the experimental parameters has been achieved, with respect to Ref. [3]. In addition, the  $\Delta E_{01}$  ( $=22.364(1)$  MHz) has been precisely determined from the fit, the rotational constants have been obtained separately for the two tunneling states, and all quartic centrifugal distortion constants have been fitted.

We investigated then the rotational spectra of the five possible  $^{13}\text{C}$ -monosubstituted isotopologues, in natural abundance. Four of these isotopologues have a concentration of ca. 2% of that of the most abundant species, because concern the substitution of one of two equivalent carbon atoms ( $^{13}\text{C}1$  or  $^{13}\text{C}3$ ,  $^{13}\text{C}4$  or  $^{13}\text{C}9$ ,  $^{13}\text{C}5$

Table 1

Spectroscopic parameters of the parent species of indan. Single values are common to both states  $\nu = 0$  and  $\nu = 1$ .

	$\nu = 0$	$\nu = 1$
A (MHz)		3531.0444(7) <sup>a</sup>
B (MHz)	1498.3739(1)	1498.3750(1)
C (MHz)	1082.8714(1)	1082.8724(1)
$D_J$ (Hz)		32.2(7)
$D_{JK}$ (Hz)		52(4)
$D_K$ (kHz)		0.6(1)
$d_1$ (Hz)		-7.1(4)
$d_2$ (kHz)		-2.9(3)
$\Delta E_{01}$ (MHz)		22.364(1)
$\sigma/\sigma_{\text{exp}}^b$		1.3
$N^c$		242

<sup>a</sup> Error in parentheses in units of the last digit.

<sup>b</sup> Root-mean-square deviation of the fit, referred to an estimated measure errors of 3 kHz and of 50 kHz for the transition frequencies of this investigation and for those of Ref. [3], respectively.

<sup>c</sup> Number of lines in the fit (81 from the present work and 161 from Ref. [3]).

or  $^{13}\text{C}8$ ,  $^{13}\text{C}6$  or  $^{13}\text{C}7$ ), while the fifth isotopologue ( $^{13}\text{C}2$ ) is only 1%. A portion of the spectrum displaying the  $3_{12} \leftarrow 2_{11}$  transitions of the parent and  $^{13}\text{C}$  isotopologues in natural abundance is shown in Fig. 2. All rotational transitions are also reported in the Supplementary Material. They have been fitted in the same way as the normal species, supplying the spectroscopic constants of Table 2, where also the number of measured transitions is given. Due to the low number of experimental frequencies, the centrifugal distortion parameters have been fixed to the values of the normal species.

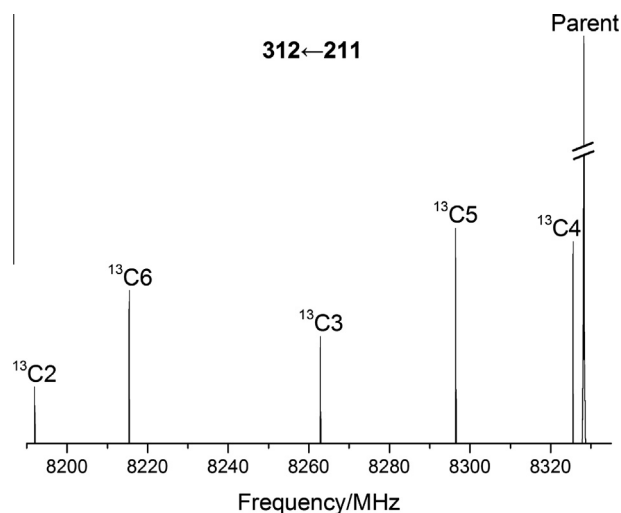


Fig. 2. Portion of the spectrum with the  $3_{12} \leftarrow 2_{11}$  transitions of the parent and  $^{13}\text{C}$  isotopologues in natural abundance.

Table 2

Experimental spectroscopic parameters of the  $^{13}\text{C}$  isotopologues (measured in natural abundance) of indan. Centrifugal distortion constants and the tunneling splitting have been fixed to the values of the parent species.

	A (MHz)	B (MHz)	C (MHz)	$\sigma^b$ (kHz)	$N^c$
$^{13}\text{C}1$ (or $^{13}\text{C}3$ )	3494.71(1) <sup>a</sup>	1486.9640(3)	1073.5820(2)	0.9	9
$^{13}\text{C}2$	3529.16(1)	1472.0361(3)	1069.2427(2)	0.6	9
$^{13}\text{C}4$ (or $^{13}\text{C}9$ )	3519.11(1)	1498.2566(3)	1081.7008(2)	0.6	9
$^{13}\text{C}5$ (or $^{13}\text{C}8$ )	3483.37(1)	1493.8816(3)	1076.0163(2)	0.8	9
$^{13}\text{C}6$ (or $^{13}\text{C}7$ )	3519.39(1)	1476.9880(3)	1070.5935(2)	0.9	9

<sup>a</sup> Standard error in parentheses in units of the last digit.

<sup>b</sup> Standard deviation of the fit.

<sup>c</sup> Number of fitted transitions.

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