

Synchrotron-Based Rotationally Resolved High-Resolution FTIR Spectroscopy of Azulene and the Unidentified Infrared Bands of Astronomy**

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Dedicated to Klaus Hafner on the occasion of his 85th birthday

In part, because of its blue color azulene (Figure 1) and its derivatives have been the subject of spectroscopic investigation starting with the early identification of its spectrum in relation

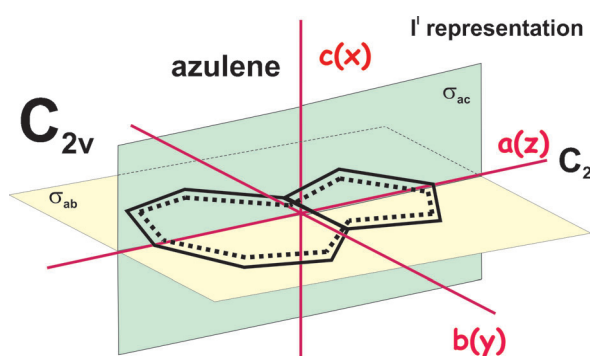


Figure 1. The molecule azulene, $C_{10}H_8$, in its molecule-fixed center-of-mass axis system including the point group symmetry operations (see Table 1). The representation is l' and the axis definitions in C_{2v} correspond to the labeling of the normal modes.

Table 1. Character table for the C_{2v} and M_{24} symmetry groups of azulene^[32–34] with conventional definitions of the symbols. $\Gamma(S^*)$ gives the symmetry species in the subgroup $S^* = (E, E^*)$ isomorphous to C_s . K_a and K_c are the even (e) or odd (o) rotational quantum numbers in the totally symmetric vibrational state and g is the nuclear spin statistical weight.

C_{2v}	M_{24}	E	C_2	σ_{xz}	σ_{yz}	$\Gamma(S^*)$	J	$K_a K_c$	g
		E	$(\alpha\beta)$	$(\alpha\beta)^*$	E^*				
A_1	A^+	1	1	1	1	A^+	z	ee	56
A_2	A^-	1	1	-1	-1	A^-	J_z	eo	56
B_1	B^-	1	-1	1	-1	A^-	J_y	oo	72
B_2	B^+	1	-1	-1	1	A^+	J_x	oe	72

to the Fraunhofer spectrum by Gladstone^[1] shortly after the development of atomic spectroscopy by Bunsen and Kirchhoff^[2,3] leading finally to the discovery of its structure as an

isomer of naphthalene, but with ten π electrons in connected 5- and 7-membered ring systems by Pfau and Plattner^[4–6] (see refs. [7–10] for some of the history and literature). Hafner's synthesis^[11,12] has made the compound widely accessible. Its exceptional photophysics with fluorescence from the second excited singlet state S_2 violating Kasha's rule was studied by Beer and Longuet Higgins^[13] and its intramolecular dynamics including isomerisation to naphthalene after electronic (UV/Vis) excitation has been studied in molecular beams,^[14,15] shock waves^[16] and by femtosecond pump-probe techniques.^[17] High-resolution spectra have been extensively analysed in the microwave^[18–21] and recently in the UV range.^[22]

While there is a vast literature on vibrational, Raman and, in particular, infrared spectra starting in 1949,^[9,10] these spectra have so far defeated analyses at high resolution. In our work we have achieved the first high-resolution rotational-vibrational analysis of the infrared spectrum of azulene. This has become possible using synchrotron-based highest-resolution Fourier transform infrared (FTIR) spectroscopy^[23,24] in combination with pattern-recognition methods of analysis.^[25] We present an analysis of the infrared spectrum of azulene covering its strongest fundamental ν_{44} and a new determination of the ground-state A rotational constant as well as the quartic constants using combination differences (CD) calculated from the infrared data. This is of general importance for a deeper understanding of the dynamics of azulene upon excitation and its spectroscopy in the electronic ground state. In addition, the IR spectra of polycyclic aromatic hydrocarbon (PAH) molecules, such as azulene and naphthalene, recently gained special interest in the context of the interstellar unidentified infrared bands (UIBs, sometimes also called UIRs).^[23,26] We have thus extended our previous investigations of the high-resolution infrared spectra of the bicyclic compounds naphthalene,^[23] biphenyl^[27] and indole^[23] to azulene.

The infrared spectra of such aromatic compounds are difficult to measure and to resolve, owing to the low vapor pressure and the tiny rotational constants of these molecules. However, the use of brilliant synchrotron radiation in the infrared region^[23,28] and of very high resolution interferometers^[29,30] rotationally resolved FTIR now makes it possible to explore the spectroscopy and dynamics in the FIR/THz regime of such large carbon ring systems of aromatic and non-aromatic character in the gas phase at room temperature.^[23,31] As we have shown^[23] there is a coincidence of the naphthalene band at 12.8 μm and one of the UIBs.

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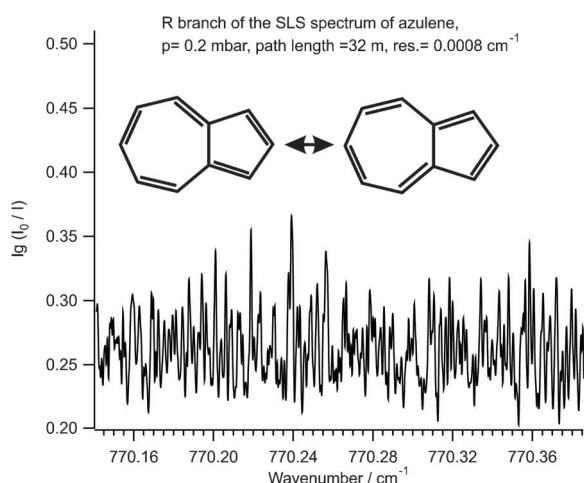
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[**] FTIR = Fourier transform infrared spectroscopy

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Thus, the question of related coincidences with spectra of azulene seems pertinent. A further question of interest concerns the structure and symmetry of azulene. There has been some debate of symmetry breaking from C_{2v} to C_s symmetry on the basis of ab initio calculations,^[35,36] now experimentally resolved on the basis of a recent analysis of microwave spectra.^[20] However, the question of symmetry breaking towards effective C_s symmetry and by out-of-plane bending even to chiral structures with C_1 symmetry in excited vibrational and, more likely, electronic states remains pertinent. Table 1 provides the character table of relevant symmetry groups C_{2v} (point group symmetry) isomorphous to the molecular symmetry group M_{54} .^[32–34] From Table 1 one can read the reduction to the group S^* (isomorphous to C_s). If the A^+ and A^- levels become degenerate in an effectively non-planar C_1 -type structure, such a state might become even of interest for experimental schemes to measure molecular parity violation.^[33]

FTIR spectra of azulene were recorded with the ETH-SLS Bruker prototype 2009^[23] using synchrotron radiation in the range of 600 to 900 cm^{-1} in a White-type cell with path lengths ranging from 3.2 to 19.2 m. The strongest band is the ν_{44} fundamental shown in Figures 2 (upper part) and 3. The



Loomis-Wood diagram of the ν_{44} fundamental of azulene (R branch).

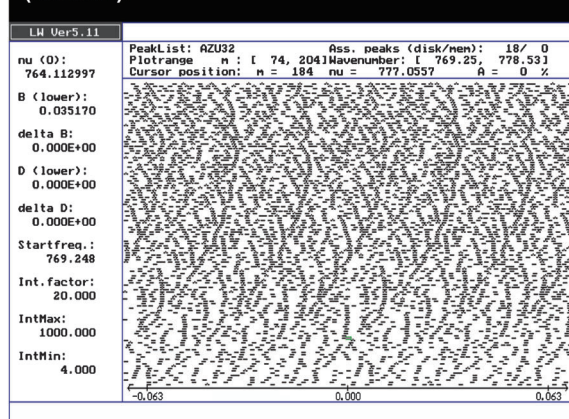


Figure 2. Top: Part of the R branch of the ν_{44} fundamental of azulene. Bottom: Loomis-Wood diagram of the R branch. The wavenumbers are plotted against $(B+C)/2$.

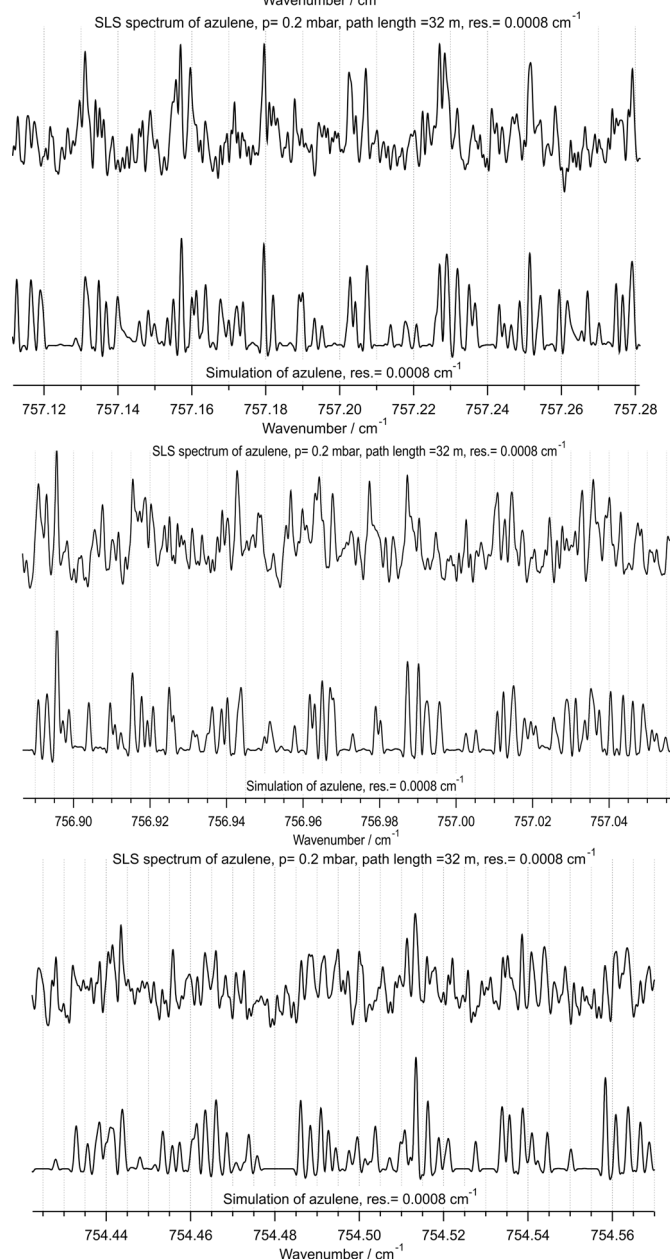
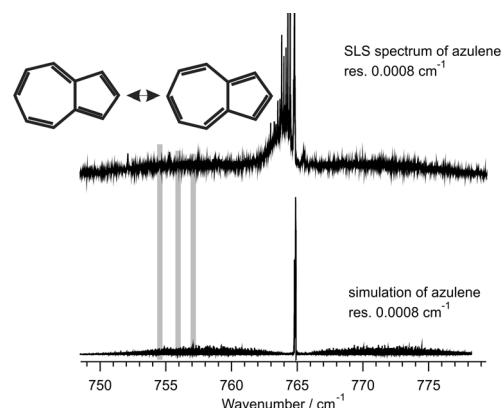


Figure 3. Top: SLS-FTIR spectrum of the ν_{44} fundamental of azulene. The upper trace is the experimental spectrum and the lower trace the simulation. Lower panels: Enlargements of P branch regions in the azulene spectrum.

ETH- SLS Bruker 2009 prototype has an unapodized resolution of 0.00053 cm^{-1} (16 MHz). Apertures from 1.15 mm to 0.8 mm allowing an effective resolution of 0.0007 cm^{-1} were applied. The sample pressure varied from 0.02 to 0.1 mbar. The Doppler width is about 0.008 cm^{-1} and the pressure broadening is estimated to be smaller.

Using C_{2v} symmetry for azulene the a axis is identical with the C_2 axis, as shown in Figure 1. The molecule has 48 normal modes classified as $17a_1$, $16b_2$, $6a_2$ and $9b_1$. The symmetric in-plane a_1 modes generate a -type bands, the in-plane b_2 modes generate b -type bands and the out-of-plane b_1 modes generate c -type bands. The out-of-plane a_2 modes are infrared inactive. The ν_{44} band is of b_1 symmetry and shows c -type transitions in the spectrum.

The assignment of the observed rovibrational transitions belonging to the P and R branches were carried out with a Loomis–Wood assignment program.^[25,37–40] Figure 2 shows part of the R branch of the ν_{44} fundamental. No obvious structure is visible. However, a representation of the wavenumbers as a function of the rotational constants $(B+C)/2$, denoted as a Loomis–Wood diagram and shown in the lower part of Figure 2, makes the patterns visible in the spectrum. Based on these patterns an assignment of the lines is possible. The nuclear spin statistical weights in the totally symmetric ground state result in the intensity ratios $ee : eo : oo : oe = 7:7:9:9$ for $K_a K_c$ even or odd and can be observed in each K_c series as an alternation of the transition intensity depending on the K_a value, in principle. The advantage of c -type transitions consists of the observation of nuclear spin statistical weights even at a non-resolved asymmetry splitting. However, due to the congested spectrum of azulene and the intensity ratios close to one it is difficult to detect the nuclear spin statistical weights, under our conditions.

The rovibrational analysis was carried out with Watson's A reduced effective Hamiltonian^[41] in the I' representation (see the Supporting Information) up to quartic centrifugal and sextic distortion constants. The spectroscopic data were analysed using the WANG program.^[42] First, the ground-state constants of azulene listed in Table 2 were determined using the

microwave lines (115 lines) from refs. [20,21] and the CDs (619) calculated from the assigned infrared absorption lines. As start values the values from ref. [21] (Table 2) were used. The $\Delta_{JK}\delta_J\delta_K$ of the ground state were held fixed to the values of ref. [21] to minimize correlations. The use of CDs including higher J numbers allowed us to determine new values for the quartic Δ_J and Δ_K and sextic Φ_{JK} and Φ_{KJ} constants of the ground state. Second, the spectroscopic constants of the ν_{44} state of azulene listed in Table 2 were determined. During the fitting procedure for ν_{44} the constants of the ground state as well as the values of the quartic constants Δ_{JK} and δ_J were held fixed at the ground-state values from ref. [21]. As one can see, the rotational constants do not change dramatically upon excitation of the out-of-plane mode and the quartic constants change only slightly. The ν_{44} fundamental of azulene was simulated using the constants in Table 2 and the nuclear spin statistical weights. Figure 3 (lower parts) shows the comparison of measured parts of the P branch region of the ν_{44} fundamental (middle and lower part, upper trace) with a simulation (middle and lower part, second trace). Differences between the simulated and measured spectrum result from the presence of numerous hot bands and ^{13}C isotopomers. The ground-state population of azulene at 296 K is only about 12%. The advantage of the analysis of the highly-resolved spectra consists of the simulation of these spectra at any temperature even at very low temperature, as observed in the interstellar medium where the vibrational ground state dominates. Naphthalene and azulene are among the simplest polycyclic aromatic hydrocarbons,^[21] strictly speaking bicyclic compounds, and therefore the understanding of their IR spectrum might be a first step in the identification of the UIBs. We have shown that there is a coincidence between the naphthalene band at $12.8\text{ }\mu\text{m}$ and one of the UIBs,^[23] as shown in Figure 4. If we consider the azulene band shifted to $13.2\text{ }\mu\text{m}$ we can see that there is no UIB in this range (Figure 4). In order to extend the search for possible carriers consisting of a bicyclic system we also measured the IR spectrum of biphenyl.^[27] This compound has two major absorption features at 13.55 and $14.3\text{ }\mu\text{m}$ in the range from 600 to 1000 cm^{-1} which are by far the strongest IR bands.^[27] A

comparison of these biphenyl bands with UIBs measured in the 13 to $15\text{ }\mu\text{m}$ range^[26,43] illustrate coincidences as described in ref. [27]. A summary of the possible coincidences of azulene, naphthalene, indole and biphenyl bands with UIBs is listed in Table 3.

Although we have to consider that UIBs are generally emission bands, whereas the herein presented spectra are absorption bands, we have previously shown that there is no dramatic difference in intensity between measured naphthalene emission bands^[45] and our recorded ab-

Table 2. Experimental rovibrational parameters of the ground state and the ν_{44} state of azulene.

	Ground state ^[21]	Ground state ^[a]	ν_{44} ^[a]
$\tilde{\nu}$ [cm^{-1}]	0	0	764.873814 (23)
A [cm^{-1}]	0.0947973231 (60)	0.09478538 (27)	0.094754491 (32)
B [cm^{-1}]	0.04185706061 (76)	0.04185705 (90)	0.04182878 (68)
C [cm^{-1}]	0.02904385226 (67)	0.02904873 (81)	0.02906392 (93)
Δ_J [10^{-9} cm^{-1}]	0.75145 (73)	1.68 (14)	1.588(11)
Δ_{JK} [10^{-9} cm^{-1}]	1.1824 (47)	1.1824 ^[b]	1.1824 ^[b]
Δ_K [10^{-9} cm^{-1}]	6.314 (10)	4.69 (17)	4.837 (16)
δ_J [10^{-9} cm^{-1}]	0.25108 (27)	0.25108 ^[b]	0.25108 ^[b]
δ_K [10^{-9} cm^{-1}]	2.255 (17)	2.2546 ^[b]	3.163 (89)
Φ_{JK} [10^{-15} cm^{-1}]		152 (29)	140.1 (25)
Φ_{KJ} [10^{-15} cm^{-1}]	-0.791 (83)	-213 (34)	-191.6 (33)
N_{data}	115	734 (115 + 619)	4040
J_{max}	59	89	97
d_{rms} [cm^{-1}]	0.00000087	0.00025	0.00023

[a] This work. [b] These parameters are fixed to the ground state values of ref. [21].

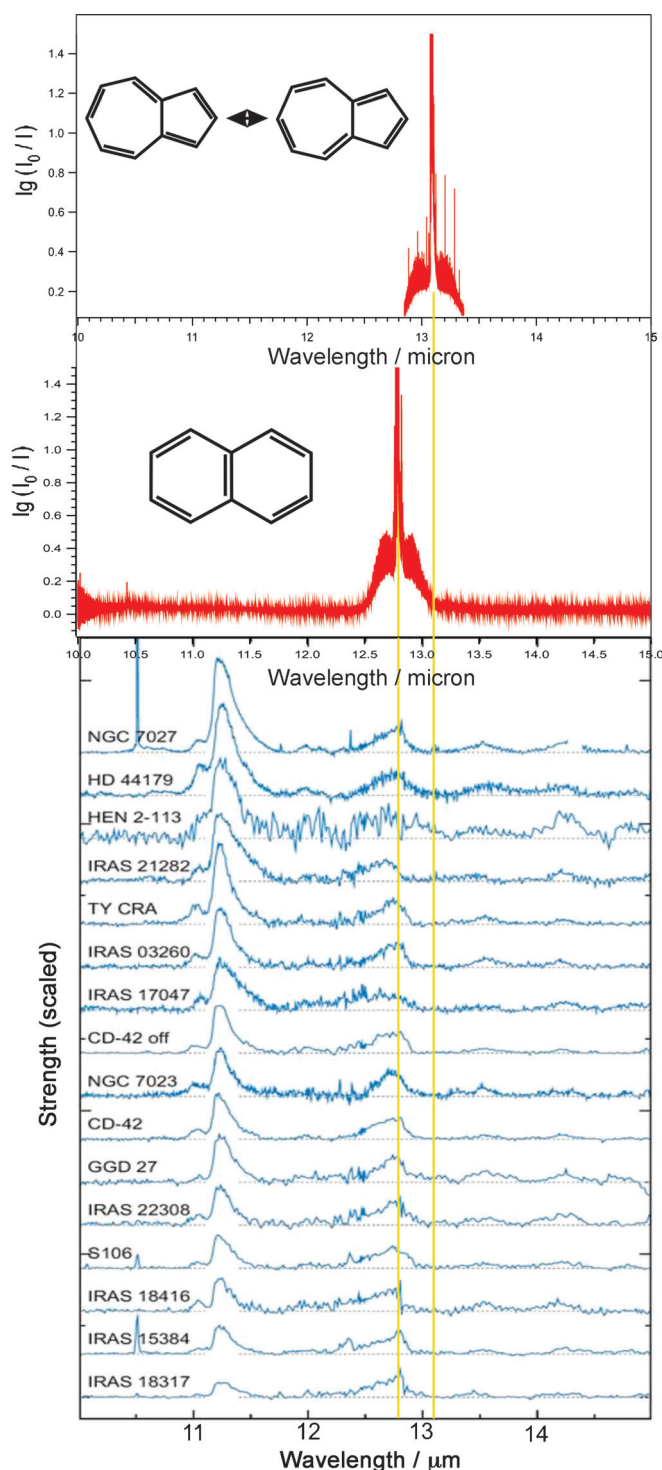


Figure 4. Comparison of the recorded spectrum of azulene (top) and naphthalene^[23] (middle) with UIBs from refs. [26] and [43].

sorption bands in the 3 μm region. The coincidences found so far concern weak UIBs. Therefore, the search for carriers presenting strong UIB features at 3.3, 6.2, 7.7, 8.6 and 11.3 μm remains open.^[26]

High-resolution spectroscopy with rotational vibrational line analysis is the way to proceed in the future, as simulations become possible at various low temperatures. We have ach-

Table 3. Survey of coincidences of strong bands with unidentified interstellar bands (UIBs) (+ indicates coincidence, – lack of coincidence).

	λ [μm]	11.25	12.8	13.55	14.6
UIB	$\tilde{\nu}$ [cm^{-1}]	889	781	738	685
	ν [THz]	26.7	23.4	22.1	20.5
Naphthalene		–	+	–	–
Indole		–	–	–	–
Biphenyl		–	–	+	+
Azulene		–	–	–	–

ieved this here on the basis of room-temperature spectra and note the recently measured IR-CRD spectra of pyrene using supersonic jets.^[46] The present findings summarized in Table 3 exclude azulene as a strong contributor for UIBs between 10 and 15 μm .

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Keywords: azulene • biphenyls • high-resolution IR spectroscopy • synchrotron radiation • unidentified infrared bands (UIBs)

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