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# The jet-cooled $S_0 \rightarrow S_1$ excitation spectrum of 1,6-epoxy-[10]annulene

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## Abstract

The excitation spectrum of 1,6-epoxy-[10]annulene in the region of the lowest electronic transition ( $\approx 417\text{--}390\text{ nm}$ ) has been measured under supersonic expansion conditions. The observed vibronic structure, with onset at  $24\,008\text{ cm}^{-1}$ , is discussed mostly in terms of allowed transitions. Comparison with MCSCF/CAS calculations of vibrational frequencies in  $S_0$  and  $S_1$  allows the assignment of several excited state fundamentals and correlation with ground state modes. Both the experimental and theoretical results point to the conclusion that equilibrium geometry changes upon excitation, with the  $C_1$  and  $C_6$  atoms of the molecular ring, connected by the epoxy bridge, moving slightly apart going from  $S_0$  to  $S_1$ . © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Supersonic molecular expansions have long been used to investigate the dynamical properties of isolated collision-free molecules and weakly bound complexes [1]. Because of expansion, the molecular distribution among translational and rotational levels narrows dramatically with effective suppression of band broadening. This makes the structure of electronic spectra considerably simpler. On the other hand, van der Waals clusters with rare gas atoms or small molecules may also be

formed during expansion, thus allowing us to study the solvation effects and energy transfer phenomena in prototype systems.

The spectroscopy of aromatics has been thoroughly investigated since the introduction of the technique [2–10] and, as a result, a detailed knowledge of the vibronic structure in the manifold of lowest excited singlets has been obtained. More complex time-domain experiments of rotational coherence [11,12] and ultrafast intramolecular vibrational energy redistribution [13,14] were then possible by exciting into well-defined energy levels.

Monocyclic bridged  $[4n + 2]$ annulenes ( $n \geq 2$ ) are a promising class of compounds to which these experiments may be extended. While unsubstituted

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annulenes do not exist in a planar conformation due to steric hindrance between hydrogen atoms and/or ring torsional strain, a planar (or almost planar) structure is possible if triple bonds along the cycle or suitable bridgehead groups between opposite ring C atoms are inserted [15]. Having the cycle  $(4n + 2) \pi$  electrons, the corresponding systems are considered higher homologues of benzene and share with benzene distinctive aromatic properties such as the absence of bond length alternation or, in other words, a ground state equilibrium geometry associated with the most symmetrical conformation [16]. However, the presence of the bridge makes the two ring sides non-equivalent, in contrast with the more common aromatics. This suggests surface selectivity for cluster formation. Moreover, the bridge itself may be a linking site depending on the nature of the bridging atoms and of the second cluster component.

With these considerations in mind and having been involved in the recent past in high resolution studies of van der Waals complexes [17–20] we

wish to undertake a research project on bridged  $[4n + 2]$ annulenes aimed at characterizing the spectroscopy of these systems and of their van der Waals complexes. Here we report preliminarily on the  $S_0 \rightarrow S_1$  fluorescence excitation spectrum of 1,6-epoxy-[10]annulene (see Fig. 1) under supersonic jet expansion. The study is intended to stand as background information on  $S_1$  vibronic levels necessary to discuss future experiments on cluster aggregates.

## 2. Experimental

1,6-Epoxy-[10]annulene of gas-chromatographic purity was generously supplied by Prof. Vogel (University of Köln, Germany).

The experimental apparatus for jet spectroscopy has been assembled during this work. A solenoid pulsed valve and controller (General Valve, series 9) are operated with variable opening duration (usually 250  $\mu$ s to ensure a complete opening) by means of a Teflon poppet moving against the nozzle hole, 0.35 mm diameter, to generate relatively cold molecular beams under supersonic expansion [21]. The valve is connected to a gas line and to a glass side arm containing the solid sample of 1,6-epoxy-[10]annulene. The valve assembly, the sample holder and the interconnecting metal tubing may be heated up to 150°C by a resistive wire, 1 m long ( $50 \Omega \text{ m}^{-1}$ , 1 A max current). In our case, setting the temperature to 50°C the sample vapour pressure guarantees a sufficiently high molecular density inside the beam for the experiment. The expansion chamber, 150 mm diameter with six flanges mounted along three perpendicular axes, is evacuated with a diffusion pump (Edwards DIFFSTAK, 700  $\text{l s}^{-1}$  pumping speed) and a rotary pump. The chamber pressure is typically lower than  $10^{-4}$  mbar with He backing pressure up to 3 bar and with the valve nozzle arranged looking downward to the pump inlet to enhance the operation efficiency.

The laser beam, after entering the vacuum chamber through a quartz window at Brewster angle, is focused with an  $f = 500$  mm lens at the crossing point with a molecular jet, 5 mm away from the nozzle. The fluorescence emission is col-

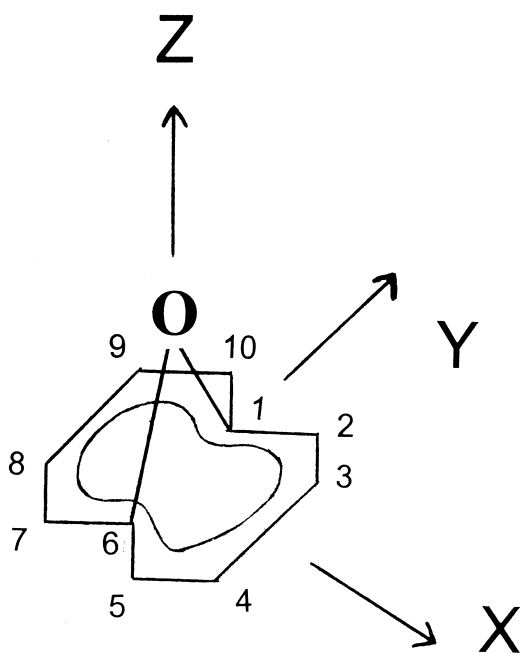


Fig. 1. The molecular structures of 1,6-epoxy-[10]annulene with atomic numbering and the reference axis system.

lected by an  $f = 25$  mm  $f/1$  quartz lens in a direction normal to both the laser and the molecular beam. To reduce the amount of scattered radiation the laser path inside the chamber has been extensively baffled and the compartment walls coated with a graphite film. The collimated fluorescence emission leaves the chamber through a silica window, is focused by an  $f = 50$  mm  $f/1$  lens and spatially filtered through a variable iris (typically, 3–5 mm opening size) placed in the lens' focal plane.

Exciting light in the 24 000–25 600  $\text{cm}^{-1}$  range ( $\approx 417$ –390 nm) was provided by frequency mixing the output from a nanosecond DCM special and DCM dye laser with the Nd:YAG fundamental. Pulse energies in the range 5–50  $\mu\text{J}$  were used without any evidence of saturation effects. The temporal resolution of our detection system was  $\approx 10$  ns, as estimated from the decay signal of the incident scattered radiation. For alignment purposes and to set the timing of the experiment a pulsed naphthalene beam was first excited with the fourth harmonic of the Nd:YAG laser at 266 nm. The  $S_0 \rightarrow S_1$  excitation spectrum of 1,6-epoxy-[10]annulene was measured in steps of 0.25 Å of dye laser scan. The fluorescence signal was filtered through a cut-off filter (65–1300, Rolyn Optics), detected by the photomultiplier and averaged by a boxcar (typically, 10 pulses avg.) gated for a maximum  $S/N$  ratio with a time delay of 10 ns relative to the excitation pulse and a gate width of 60 ns. The output was normalized to the incident intensity and background subtracted (if needed). An averaging process with a larger  $S/N$  ratio was necessary in the first part of the spectrum ( $\approx$  up to 24 300  $\text{cm}^{-1}$ ) to detect the weak hot band structure. It was not possible to extend the measurement below 23 900  $\text{cm}^{-1}$  due to leaking of incident radiation through the cut-off filter.

The fluorescence lifetimes exciting the strongest vibronic peaks were measured. After deconvolution with the instrumental function all the observed decay profiles were found to be monoexponential with time constants equal to  $20 \pm 1.5$  ns. As an example, we report in Fig. 2 the fluorescence decay following excitation into the 25 655  $\text{cm}^{-1}$  vibronic band of the  $S_1$  state superimposed with the instrumental time response.

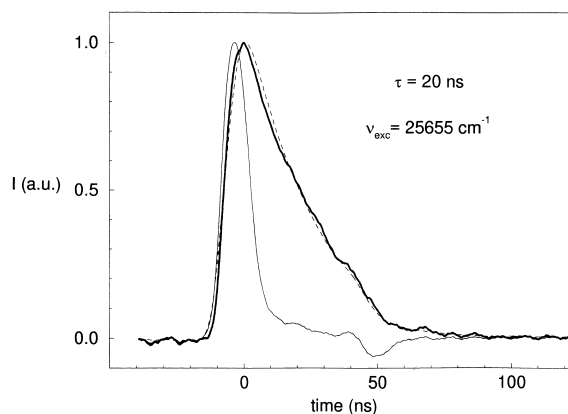


Fig. 2. Fluorescence decay (heavy full line) of 1,6-epoxy-[10]annulene under supersonic jet expansion exciting at 25 655  $\text{cm}^{-1}$  (1647  $\text{cm}^{-1}$  from the electronic origin). The instrumental response (light full line) and the convoluted profile with a monoexponential decay process (dashed line) are also shown. The fluorescence lifetime  $\tau$  is found to be 20 ns.

### 3. Results

The excitation spectrum of 1,6-epoxy-[10]annulene has been measured under supersonic expansion conditions in the region of the first electronic transition. The spectrum may be divided into two parts (see Figs. 3 and 4) to make the discussion easier. The first part, ranging from 23 900 to 24 600  $\text{cm}^{-1}$ , shows relatively few and well-spaced bands while the second, up to 25 650  $\text{cm}^{-1}$ , has increased spectral congestion, mostly due to Franck–Condon progressions. According to calculations of the next section and similar to the 1,6-methano[10]annulene [22] and naphthalene [23] cases, the transition is allowed, long-axis polarized, i.e.,  $S_0(A_1) \rightarrow S_1(B_1)$  assuming  $C_{2v}$  symmetry for both states. Vibronic activity is in principle expected only for  $a_1$ ,  $a_2$  and  $b_1$  modes.

#### 3.1. The 23 900–24 600 $\text{cm}^{-1}$ region

The electronic origin, observed at 24 008  $\text{cm}^{-1}$ , is the strongest  $S_0 \rightarrow S_1$  peak (see Fig. 3, upper). On the low energy side, two weak bands occur at  $-16$  and  $-57$   $\text{cm}^{-1}$  from the origin. The same pattern is found for the 290  $\text{cm}^{-1}$  band and, partly, for the 157 and 484  $\text{cm}^{-1}$  bands, suggesting

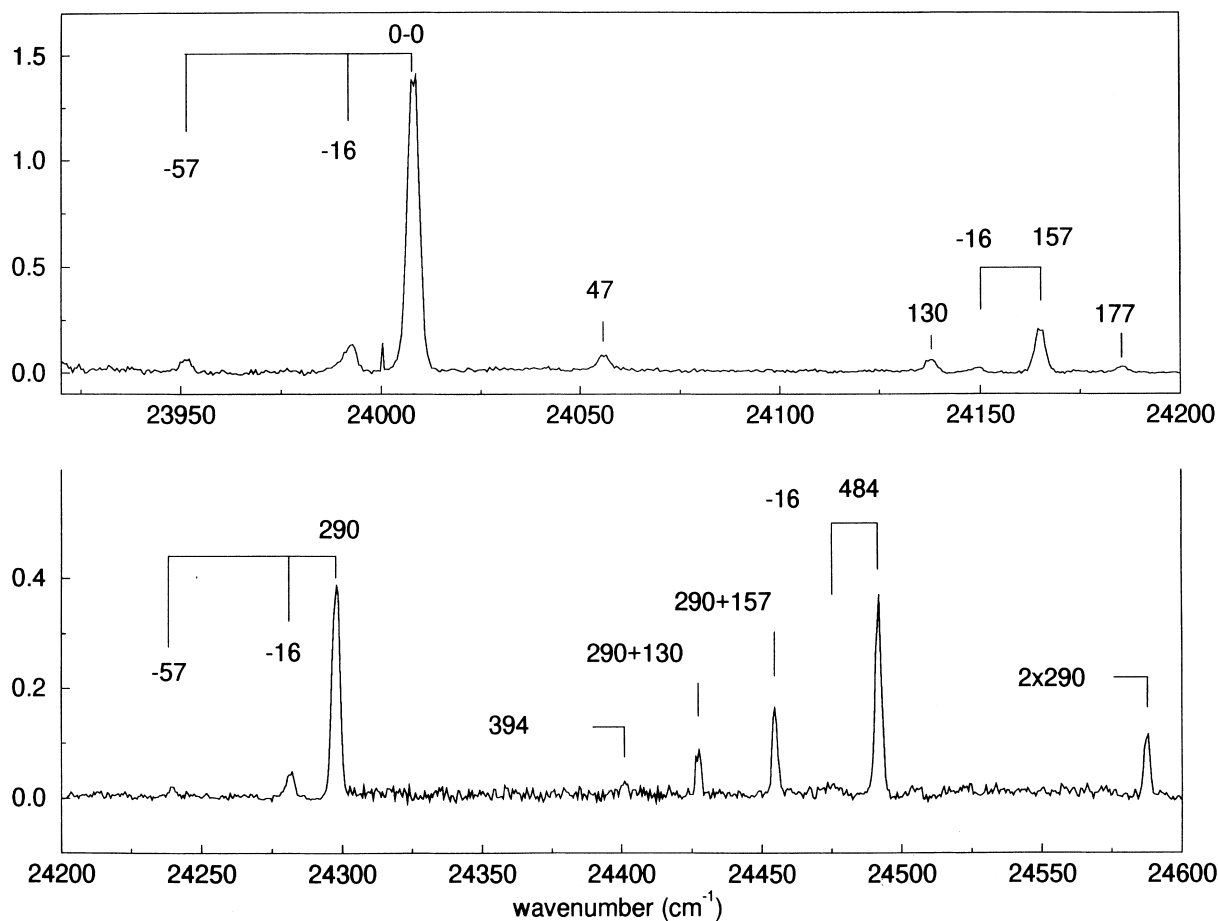


Fig. 3. The  $S_0 \rightarrow S_1$  fluorescence excitation spectrum of 1,6-epoxy[10]annulene under supersonic jet expansion in the region 23900–24600  $\text{cm}^{-1}$ . The peak frequencies ( $\text{cm}^{-1}$ ) with respect to the electronic origin, 24008  $\text{cm}^{-1}$ , are shown.

the occurrence of hot transitions from torsional ground state levels of 1,6-epoxy[10]annulene, significantly populated at the vibrational temperature of the sample. The vibrational spectra of 1,6-epoxy[10]annulene have been recently reported and assigned [24]. In particular, no mode was either observed or calculated below 140  $\text{cm}^{-1}$ . Experimentally [24], the two lowest mode, of  $a_2$  and  $a_1$  symmetry, respectively, fall at 176 and 189  $\text{cm}^{-1}$ . Thus, an assignment of our hot bands as (1–0) transitions may be excluded. Considering the next possibility, i.e. (1–1), we first note that these bands are red-shifted with respect to the corresponding main peaks, so that the modes should have  $S_1$  frequencies necessarily lower than

in  $S_0$ . Also, within this hypothesis the (1–1)–(0–1) gap is for a given mode equal to its ground state frequency. Spectral inspection reveals that both these conditions are satisfied if we couple in the (0–0) region the  $-16 \text{ cm}^{-1}$  with the  $157 \text{ cm}^{-1}$  peak and the  $-57 \text{ cm}^{-1}$  with the  $130 \text{ cm}^{-1}$  peak. The two differences, 173 and 187  $\text{cm}^{-1}$  are in good agreement with the already mentioned ground state values. The 290  $\text{cm}^{-1}$  band is easily assigned as the  $S_1$  counterpart of the 318  $\text{cm}^{-1}$   $a_1$  fundamental, which shows strongly in the Raman spectrum [24]. Other peaks (419, 447, 580  $\text{cm}^{-1}$ ) are combinations (290 + 130, 290 + 157  $\text{cm}^{-1}$ ) and first overtone of the 290  $\text{cm}^{-1}$ . The weak 394  $\text{cm}^{-1}$  band is probably related to the  $a_2$

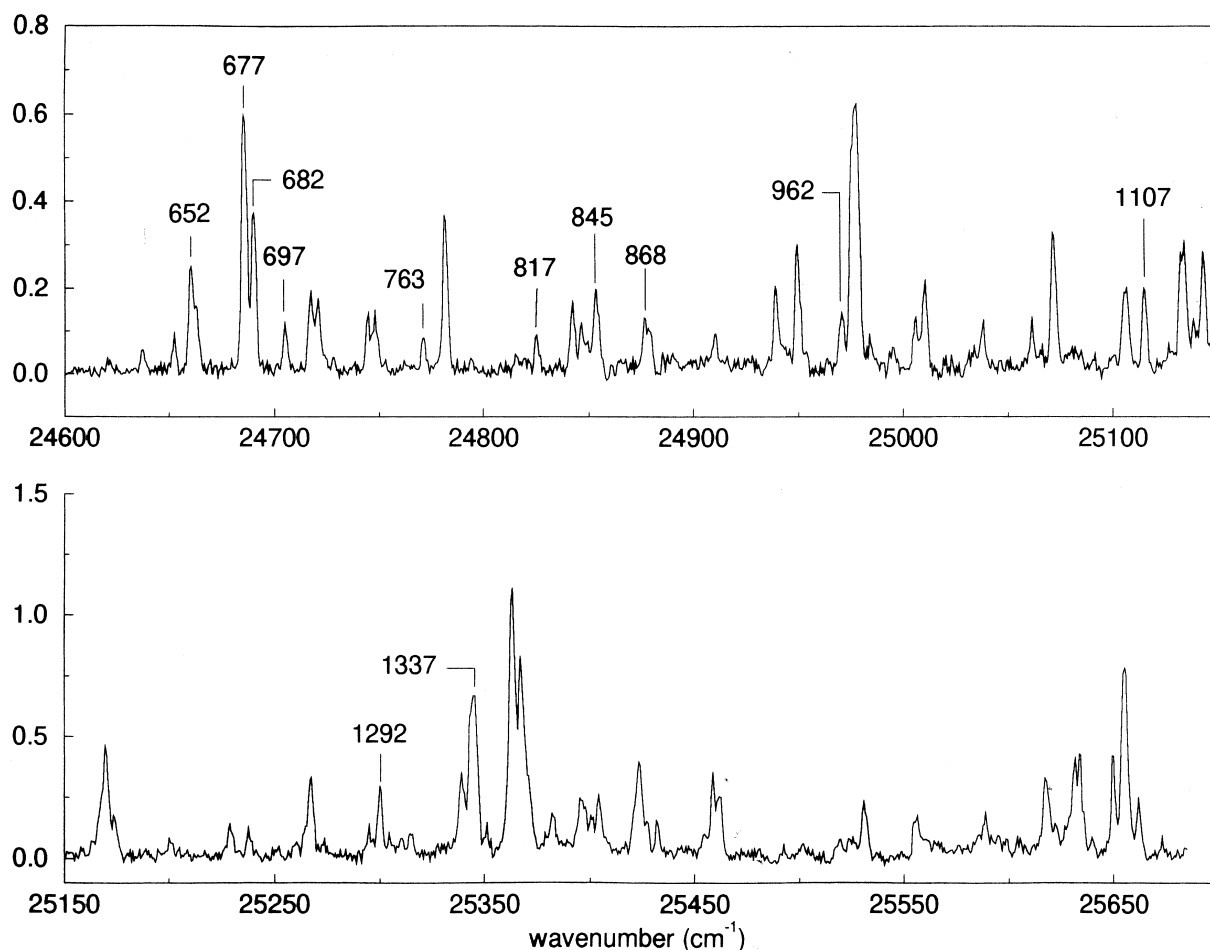


Fig. 4. The  $S_0 \rightarrow S_1$  fluorescence excitation spectrum of 1,6-epoxy[10]annulene under supersonic jet expansion in the region 24600–25650  $\text{cm}^{-1}$ . Only the frequencies ( $\text{cm}^{-1}$ ) of fundamentals with respect to the electronic origin, 24008  $\text{cm}^{-1}$ , are shown.

ground state 411  $\text{cm}^{-1}$  mode [24]. There are two additional bands of weak intensity, 47 and 177  $\text{cm}^{-1}$ , and one strong, 484  $\text{cm}^{-1}$ , whose assignment is not straightforward on a simple correlation basis.

### 3.2. The 24600–25650 $\text{cm}^{-1}$ region

As clearly shown in Fig. 4, the number of observed peaks increases appreciably  $\approx 600 \text{ cm}^{-1}$  above the electronic origin. Due to evident difficulties in the spectral assignment of bands of medium/weak intensity, a systematic procedure has been applied in order to express high energy vib-

ronic bands as a function of those of lower energy and to find at the same time bands not reducible to any other. The latter may be considered fundamentals, of  $a_1$ ,  $a_2$  or  $b_1$  symmetry, or at most even overtones (or combinations with non-totally symmetric modes) of  $b_2$  modes. The results, collected in Table 1, show that the great majority of vibronic bands may be assigned, within a few wavenumbers, as combinations of a small number of fundamentals. Only three of them (1107, 1337 and, possibly, 1292  $\text{cm}^{-1}$ ) have been identified above 1000  $\text{cm}^{-1}$  from the origin. The strongest fundamentals occur, according to this analysis, in the region  $\approx 650\text{--}700 \text{ cm}^{-1}$ . This suggests that most of

Table 1

The  $S_0 \rightarrow S_1$  excitation spectrum of 1,6-epoxy[10]annulene in supersonic expansion: observed peaks (obs,  $\text{cm}^{-1}$ ) relative to the electronic origin at  $24008 \text{ cm}^{-1}$  and assignment (ass)<sup>a</sup>

obs	ass	obs	ass	obs	ass
–57	–189 + 130(+2)	845	845; $7a_1$	1335	682 + 652(+1)
–16	–176 + 157(+3)	868	868; $5a_2$	1337	1337; $10a_1?$
0	(0–0)	871	$3 \times 290(+1)$	1343	$763 + 2 \times 290(0)$
47	?	903	$484 + 290 + 130(-1)$	1355	$2 \times 677(+1)$
130	$130; 1a_1$	932	$484 + 290 + 157(+1)$	1359	$677 + 682(0)$
142	$-176 + 2 \times 157(-4)$	941	$652 + 290(-1)$	1363	$2 \times 682(-1)$
157	$157; 1a_2$	962	$962; 8a_1$	1374	$697 + 677(0)$
177	$47 + 130(0)$	970	$677 + 290(+3);$	1387	$677 + 2 \times 290 + 130(0);$
232	$-189 + 130 + 290(+1)$		$682 + 290(-2);$		$652 + 2 \times 290 + 157(+2)$
274	$-176 + 157 + 290(+3)$	976	$845 + 130(+1)$	1392	$2 \times 697(-2)$
290	$290; 2a_1$	987	$697 + 290(0)$	1396	$720 + 677(-3)$
394	$394; 2a_2$	998	$713 + 290(-5)$	1415	$677 + 2 \times 290 + 157(+1);$
419	$290 + 130(-1)$	1002	$845 + 157(0)$		$739 + 677(-1);$
447	$290 + 157(0)$	1026	$3 \times 290 + 157(-1)$		$763 + 652(0)$
468	$-176 + 157 + 484(+3)$	1030	$739 + 290(+1)$	1419	$682 + 2 \times 290 + 157(0)$
484	$484; 3a_2$	1053	$763 + 290(0)$	1424	$652 + 484 + 290(-2)$
497	$-176 + 677(-4)$	1064	$484 + 2 \times 290(0)$	1447	$5 \times 290(-3)$
580	$2 \times 290$	1097	$677 + 290 + 130(0);$	1451	$677 + 484 + 290(0)$
613	$484 + 130(-1)$		$652 + 290 + 157(-2)$	1455	$682 + 484 + 290(-1)$
629	$629; 2 \times 1b_1$	1107	$1107; 6a_2$	1484	$677 + 652 + 157(-2);$
643	$484 + 157(+3)$	1124	$677 + 290 + 157(0);$		$2 \times 677 + 130(0)$
652	$652; 4a_1$	1131	$682 + 290 + 157(+2)$	1493	$682 + 652 + 157(+2)$
655	$655; 2 \times 1b_2$	1135	$652 + 484(-1);$	1511	$2 \times 677 + 157(0)$
677	$677; 5a_1$		$845 + 290(0)$	1515	$682 + 677 + 157(-1)$
682	$682; 4a_2$	1161	$677 + 484(0)$	1523	$845 + 677(-1)$
697	$697; 3b_1$	1166	$682 + 484(0)$	1548	$677 + 3 \times 290(+1)$
709	$2 \times 290 + 130(-1)$	1192	$845 + 290 + 157(0);$	1581	$677 + 484 + 290 + 130(0);$
713	$2 \times 2b_2$		$484 + 2 \times 290 + 130(-2)$		$652 + 484 + 290 + 157(-2)$
720	$394 + 655/2$	1220	$484 + 2 \times 290 + 157(-1);$	1610	$677 + 484 + 290 + 157(+2)$
737	$2 \times 290 + 157(0)$		$739 + 484(-3)$	1614	$682 + 484 + 290 + 157(+1)$
739	$2 \times 2b_1$	1229	$652 + 2 \times 290(-3)$	1623	$682 + 652 + 290(-1);$
763	$763; 4b_1$	1259	$677 + 2 \times 290(+2)$		$677 + 652 + 290(+4)$
774	$484 + 290(0)$	1266	$652 + 484 + 130(0)$	1625	$1337 + 290(-2)$
786	$2 \times 394(-2);$	1286	$655 + 629(+2)$	1641	$2 \times 677 + 290(-3)$
	$652 + 130(+4)$	1292	$1292?;$	1647	$677 + 682 + 290(-2)$
808	$652 + 157(-1);$		$652 + 484 + 157(-1)$	1654	$2 \times 682 + 290(0)$
	$677 + 130(+1)$	1307	$652 + 655(0)$	1665	$697 + 677 + 290(+1)$
817	$817; 6a_1$	1331	$677 + 652(+2);$		
834	$677 + 157(0)$		$845 + 484(+2)$		
838	$682 + 157(-1)$				

<sup>a</sup> The difference between the observed frequencies and combinations (or overtones) of fundamentals is reported in parentheses. Fundamentals are numbered as in Table 3.

the Franck–Condon intensities of our spectrum arise from low frequency  $a_1$  modes. However, the assignment of excited fundamentals and the correlation with ground state modes may be attempted with confidence only when making use of calculation results. The two points are analysed in more detail in the next section.

#### 4. Discussion

According to density functional results (DF/B3-LYP, 6-31G\*\* basis set), the ground state equilibrium geometry of 1,6-epoxy-[10]annulene has  $C_{2v}$  symmetry with delocalization of  $\pi$  electrons over the full 10-atom ring [24], in agreement with the

X-ray diffraction data on the crystal [25]. The calculated vibrational frequencies satisfactorily match the observed values using a single scaling factor, 0.979 [24].

Being interested here in both ground (g) and excited (e) state frequencies, it is more convenient to deal with the same calculation method for the two states. Therefore equilibrium structures and frequencies of 1,6-epoxy-[10]annulene have been determined by means of the MCSCF/CAS wave function and the 6-31G basis set, promoting 10 electrons among the 10 MO's with the largest  $p_z$  contribution from the ring C atoms. In this treatment the  $C_{2v}$  ground state geometry does not correspond to a minimum of the  $S_0$  energy surface but rather to a saddle point, the  $b_1$  mode inducing double bond localization along the ring being associated with an imaginary frequency. On the contrary, the  $C_{2v}$  equilibrium structure of the  $S_1$  state is a real minimum, all vibrational frequencies being real. As seen in Table 2, the two structures have similar C–C bondlengths and very different non-bonded 1...6 distances. As the distance between these two atoms increases in  $S_1$ , the electronic delocalization along the 10-atom ring (and then the aromatic character of the state) is also increased. With reference to the  $S_0$  data, it is worth noting that a single averaged scaling factor, 0.937, may be used to fit fairly well the MCSCF/CAS frequencies to the experimental values (except to one  $b_1$ , of course) [24]. In an attempt to scale also

the excited state MCSCF/CAS frequencies, a first approximation strategy is to apply the same factor to the  $S_1$  frequencies. The complete vibrational results, which will serve as a guideline to discuss the  $S_0 \rightarrow S_1$  vibronic assignment, are reported in Table 3.

Among  $a_1$  modes, the correlations 189(g)/130(e) and 318(g)/290(e) have already been proposed on a purely experimental basis. This agrees fairly well (see Table 3) with the calculated pairs 167(g)/148(e) and 312(g)/288(e)  $\text{cm}^{-1}$ . In general ground state  $a_1$  modes decrease their frequencies from  $S_0$  to  $S_1$ , the largest effect being on 748 and 907  $\text{cm}^{-1}$  modes (674 and 840  $\text{cm}^{-1}$ , respectively,  $S_1$  values). Exceptions are the 640 and 1538  $\text{cm}^{-1}$  modes shifting to 662 and 1569  $\text{cm}^{-1}$ . Comparing the calculation with the experimental spectrum, it should be noted that three strong peaks are observed at 652, 677 and 682  $\text{cm}^{-1}$ : reasonably two of them are associated with the calculated 674 and 662  $\text{cm}^{-1}$  modes. In addition, the 845  $\text{cm}^{-1}$  band, active in combination with 290, 484 and 677  $\text{cm}^{-1}$  may correspond to the 840  $\text{cm}^{-1}$  mode.

Further support to this assignment comes from the consideration of Franck–Condon (or allowed) intensities, which may be estimated by means of well-known procedures [26–28]. In particular, the intensity of a totally symmetric (0–1) fundamental band of frequency  $\omega$  ( $\text{cm}^{-1}$ ) with respect to (0–0) is given by  $I_{0-1}/I_{0-0} = 0.5B^2$  where  $B = 0.172 \times \omega^{0.5} \times (\mathbf{X}_{S_1} - \mathbf{X}_{S_0}) \times m^{0.5} \times L$ . In the latter expression  $\mathbf{X}_{S_1}$  and  $\mathbf{X}_{S_0}$  are row vectors of the  $3N$  equilibrium coordinates relative to  $S_1$  and  $S_0$  ( $N$  being the number of atoms in the molecule), respectively,  $m$  is the diagonal  $3N \times 3N$  matrix of the atomic masses and  $L$  the Cartesian displacement column vector of each  $a_1$  normal mode with  $3N$  components. The  $I_{0-1}/I_{0-0}$  quantities of all totally symmetric modes (except C–H stretchings) are shown in Table 4. All the ratios are smaller than unity, as experimentally observed. Only four fundamental modes (288, 662, 674 and 840  $\text{cm}^{-1}$ ) are predicted to be strongly active in the  $S_0 \rightarrow S_1$  spectrum. Their relative intensities are in fair agreement with the experiment. The two largest ratios are associated with the 287 and 662  $\text{cm}^{-1}$  modes, described as combinations of CCC–H out-of-plane motion and of the epoxide,  $C_1\text{--O--}C_6$ , bending [24] and

Table 2  
Calculated C–C distances ( $\text{\AA}$ ) and energies ( $E$ , hartree) of 1,6-epoxy-[10]annulene in the ground ( $S_0$ ) and first excited ( $S_1$ ) states in  $C_{2v}$  symmetry<sup>a</sup>

	$S_0$		$S_1$
	DFT/ B3-LYP	MCSCF/ CAS	MCSCF/ CAS
C <sub>1</sub> –C <sub>2</sub>	1.400	1.391	1.404
C <sub>2</sub> –C <sub>3</sub>	1.396	1.399	1.417
C <sub>3</sub> –C <sub>4</sub>	1.416	1.417	1.423
C <sub>1</sub> ...C <sub>6</sub>	2.214	2.273	2.365
$E$		–458.031114	–457.913250

<sup>a</sup> On the left:  $S_0$  data from DF/B3-LYP and MCSCF/CAS calculations. On the right:  $S_1$  data from MCSCF/CAS calculations. DF entries (6-31G\*\* basis set) from Ref. [24]; MCSCF/CAS entries (6-31G basis set), this work; atom numbering as in Fig. 1.



Table 3

Calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of the ground ( $S_0$ ) and first excited ( $S_1$ ) state of 1,6-epoxy-[10]annulene, according to  $C_{2v}$  symmetry and the reference axis system of Fig. 1<sup>a</sup>

		$S_0$			$S_1$	
		exp	DFT/B3-LYP	MCSCF/CAS	exp	MCSCF/CAS
$a_1$	1	189	174	167	130	148
	2	318	312	312	290	288
	3	492	488	499		484
	4	623	642	640	677	662
	5	760	753	748	652	674
	6	865	868	856	817	811
	7	912	904	907	845	840
	8	973	978	973	962	936
	9	1194	1201	1249		1234
	10	1331	1341	1386	1337	1381
	11	1442	1459	1494		1493
	12	1497	1529	1538		1569
$a_2$	1	174	145	144	157	129
	2	411	412	417	394	402
	3		601	581	484	499
	4	807	796	801	682	736
	5	883	880	934	868	882
	6		958	976		921
	7	1148	1142	1162	1107	1111
	8	1220	1227	1289		1283
	9	1458	1471	1527		1503
	10	1634	1612	1631		1660
$b_1$	1	309	325	444i		344
	2	400	401	405		386
	3	687	687	611		651
	4	744	744	742	763	756
	5		845	776		850
	6	960	963	952		900
	7	1148	1166	1088		1242
	8	1239	1243	1297		1289
	9	1319	1336	1330		1518
	10	1537	1564	1595		1994
$b_2$	1	351	349	357		335
	2	450	455	433		366
	3	641	657	622		516
	4		766	790		754
	5	846	844	846		768
	6	946	961	980		879
	7	987	993	1022		1026
	8	1116	1124	1161		1133
	9		1266	1330		1327
	10	1398	1410	1481		1452
	11		1558	1580		1515

<sup>a</sup> On the left:  $S_0$  frequencies from DF/B3-LYP and MCSCF/CAS calculations. On the right:  $S_1$  frequencies from MCSCF/CAS calculations. DF entries from Ref. [24], 6-31G\*\* basis set; MCSCF/CAS entries, 6-31G basis set. The MCSCF/CAS  $S_0$  values were fitted to the experimental values of Ref. [24] with the scaling factor 0.937.

therefore favouring the structural change from  $S_0$  to  $S_1$ . Also, the  $484\text{ cm}^{-1}$   $a_1$  mode has vanishing

allowed intensity. On this basis the  $a_1$  assignment for the strong  $484\text{ cm}^{-1}$  band is questionable.

Table 4

Franck–Condon intensities,  $I_{0-1}/I_{0-0}$ , of fundamental transitions with respect to (0–0). All totally symmetric modes,  $\nu(\text{S}_1)$  ( $\text{cm}^{-1}$ ), of 1,6-epoxy-[10]annulene (except CH stretching) are considered

$\nu(\text{S}_1)$	$I_{0-1}/I_{0-0}$
148	0.0002
288	0.522
484	0.001
662	0.673
674	0.383
811	~0
840	0.10
936	0.06
1234	0.007
1381	0.002
1493	0.001
1569	0.01

Second, the Franck–Condon intensities of  $a_1$  modes with frequency  $\geq 1000 \text{ cm}^{-1}$  are quite low. This result is consistent with our band attribution in this region, proposed in terms of combinations of lower frequency modes.

Forbidden activity comes from coupling of the  $\text{S}_1(\text{B}_1)$  state with states of  $\text{A}_1$  and  $\text{B}_2$  symmetry through  $b_1$  and  $a_2$  vibrations, respectively. Since the absorption spectrum of 1,6-epoxy-[10]annulene in the UV region has not been discussed in detail so far, it is difficult to locate the  $\text{A}_1$  and  $\text{B}_2$  states. However, a strong similarity exists between this and the spectrum of 1,6-methano-[10]annulene [29]. For the latter, evidence of non-totally symmetric vibronic bands in the  $\text{S}_0 \rightarrow \text{S}_1$  spectrum has been already given [22], presumably due to  $a_2$  modes coupling  $\text{S}_1(\text{B}_1)$  with  $\text{S}_2(\text{B}_2)$  [30]. The same should be expected in the epoxy case. Most of the forbidden intensities are ascribed to  $a_2$  modes. In particular, it may be seen from Table 3 that the 581 and  $801 \text{ cm}^{-1}$   $a_2$  fundamentals decrease in  $\text{S}_1$  to 499 and  $736 \text{ cm}^{-1}$ , respectively, and may be reasonably associated with the strong 484 and  $682 \text{ cm}^{-1}$  bands.

There are two additional points of interest in our spectrum, one relative to the number of bands observed in the region  $600\text{--}750 \text{ cm}^{-1}$  and the second to the already mentioned weak bands 47 and  $177 \text{ cm}^{-1}$ . As to the first, it is readily verified that even considering all the  $a_1$ ,  $a_2$  and  $b_1$  fundamentals and all possible combinations of lower bands

falling in this region, some peaks, 629, 655, 713 and  $720$  and  $739 \text{ cm}^{-1}$ , remain unassigned. In Table 1 an assignment is proposed where the first overtones of the lowest  $b_2$  ( $335$  and  $366 \text{ cm}^{-1}$ , calc) are responsible for the weak 655 and  $713 \text{ cm}^{-1}$  lines and, correspondingly, those of the lowest  $b_1$  ( $344$  and  $386 \text{ cm}^{-1}$ , calc) for the 629 and  $739 \text{ cm}^{-1}$  lines. The  $720 \text{ cm}^{-1}$  band may be on this basis interpreted as  $394(a_2) + 655/2(b_2) \text{ cm}^{-1}$ . As to the second point, we have at the moment no definite indication for attribution. It seems plausible to assign the  $177 \text{ cm}^{-1}$  peak as  $47 + 130 \text{ cm}^{-1}$ . As to the  $47 \text{ cm}^{-1}$  line, the tentative correlation with hot band structure preceding (0–0) and unobserved under our experimental conditions is proposed.

## 5. Conclusions

In this Letter the  $\text{S}_0 \rightarrow \text{S}_1$  fluorescence excitation spectrum of 1,6-epoxy-[10]annulene under supersonic expansion has been reported. The fine band structure is mostly related to Franck–Condon activity of totally symmetric modes. The strongest  $a_1$  fundamentals, 290 and  $677 \text{ cm}^{-1}$  in the excited state, are modes involving the bending motion of the epoxide  $\text{C}_1\text{--O--C}_6$  bridge. This indicates that the molecular geometry changes upon excitation decreasing the  $\text{C}_1\text{--C}_6$  interaction, in agreement with MCSCF/CAS calculations.

Finally, it is interesting to note that the low energy part of the spectrum has a simple and well defined band structure. On the other hand, experimental suggestions have been advanced to lower the vibrational temperature of the supersonic beam and to limit the hot band occurrence [21]. The two points are advantageous for the formation and the observation of van der Waals complexes of 1,6-epoxy-[10]annulene.

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