

# The ${}^1\Pi_u \leftarrow X\ {}^1\Sigma_g^+$ electronic spectrum of $C_5$ in the gas phase

Tomasz Motylewski, Olga Vaizert, Thomas F. Giesen,<sup>a)</sup>  
Harold Linnartz, and John P. Maier<sup>b)</sup>

*Institute for Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

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The origin and three vibronic bands of the  ${}^1\Pi_u \leftarrow X\ {}^1\Sigma_g^+$  electronic transition of linear  $C_5$  have been observed in the gas phase. The carbon chain is produced in a slit nozzle employing both discharge and ablation techniques. Cavity ring down spectroscopy is used to measure the electronic transition. The origin band is found at 510.94(1) nm, shifted 29  $\text{cm}^{-1}$  to the red of the value in a neon matrix. Intramolecular processes lead to broadening and irregularities in the rotational structure. The relation to astronomical observations is discussed. © 1999 American Institute of Physics.  
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In the last years much effort has been put to the detection of electronic spectra of carbon chains and their ions in the gas phase.<sup>1</sup> This interest is in part motivated by their relevance to astrophysics, especially to understanding the absorption features observed through diffuse interstellar clouds.<sup>2</sup> Until now up to a couple of hundred of such diffuse interstellar bands (DIBs) have been observed, primarily in the 400–900 nm region.<sup>3</sup> Carbon chains are among the appealing candidates for the carriers of such bands as was initially suggested by Douglas.<sup>4</sup> Recent direct evidence for this is the electronic  ${}^2\Pi_u \leftarrow X\ {}^2\Pi_g$  spectrum of  $C_7^-$  in the gas phase. The origin band and several vibronic bands show striking matches with DIBs.<sup>5</sup> The corresponding spectra of other anions ( $C_n^-$ ,  $n=4-11$ ) have also been observed by multiphoton detachment approaches.<sup>6-8</sup> Electronic gas phase spectra of several neutral and positively charged carbon chains have been studied in direct absorption using transient frequency modulation ( $HC_6H^+$ )<sup>9</sup> and cavity ring down spectroscopy ( $C_6H$ ,  $C_8H$ ,  $C_{10}H$ , and  $HC_6H^+$ ),<sup>10-13</sup> but did not yield any matches with already identified DIBs.

The spectra of neutral pure carbon chains are of special astrophysical interest, because electronic transitions of  $C_2$  and  $C_3$  have been observed in diffuse and translucent interstellar clouds, respectively.<sup>14</sup> In the infrared region,  $C_3$  and  $C_5$  have been detected in circumstellar shells of carbon-rich stars<sup>15</sup> and rotationally resolved vibrational transitions of chains up to  $C_{13}$  have been measured in the laboratory.<sup>16-18</sup> The  $\nu_2$  bending vibration of  $C_3$  has also been tentatively identified in dense interstellar clouds in the far IR.<sup>19</sup> The present contribution presents the first gas phase electronic spectrum of a pure carbon chain comprised of more than three atoms. Cavity ring down spectroscopy (CRDS) is used to measure the  ${}^1\Pi_u \leftarrow X\ {}^1\Sigma_g^+$  electronic absorption spectrum of  $C_5$ , which has been reported earlier in a 5 K neon matrix using mass selective deposition.<sup>20</sup> The two orders of magnitude stronger  ${}^1\Sigma_u^+ \leftarrow X\ {}^1\Sigma_g^+$  transition is expected near 210 nm,<sup>20</sup> but this region is outside the present range of the CRD

spectrometer.

In the current experiment the  $C_5$  molecules are generated in two ways. The first is essentially the same as described in Ref. 13: a planar plasma is generated by a discharge through a supersonic gas pulse (3% HCCH and 1%  $CO_2$  in Ne, 11 bar backing pressure) in the throat of a 3  $\text{cm} \times 100\ \mu\text{m}$  slit nozzle. The second is vaporization by focusing a 308 nm excimer laser beam onto a graphite rod that is mounted in the throat of a 12 mm long slit. The latter technique has been successfully used to study infrared spectra of carbon chains as long as  $C_{13}$  (Ref. 17) and has the principal advantage that only pure carbon clusters are generated. However, the combination of CRDS with graphite ablation is not straightforward as instabilities occur due to the presence of soot particles in the expansion. Nevertheless the IR absorption of  $C_5$  has already thus been detected.<sup>21</sup> Furthermore this approach has been successful in detecting the electronic spectra of a number of metal-containing clusters.<sup>22</sup>

In Fig. 1 the origin band of the  ${}^1\Pi_u \leftarrow X\ {}^1\Sigma_g^+$  electronic transition of  $C_5$  is shown. The spectrum was recorded with 0.15  $\text{cm}^{-1}$  resolution, and calibrated via  $I_2$  absorption lines, both in the discharge source using  $C_2H_2$  (a) and  $C_2D_2$  (b) as precursor, and in the ablation source (c). This proves that the observed feature arises from a pure carbon species. The rotational contour shows a strong  $Q$  branch and weak  $P$  and  $R$  branches, as expected for a  ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$  transition. Besides the  ${}^1\Pi_u \leftarrow X\ {}^1\Sigma_g^+$  origin band of  $C_5$ , three transitions to vibrationally excited levels in the upper  ${}^1\Pi_u$  state have been observed in a neon matrix,<sup>20</sup> one of them of similar intensity as the origin band. These bands—vibronic transitions  $7_0^2$ ,  $2_0^1$ , and a weak unassigned one—are also observed in the gas phase, with approximately the same relative intensity ratios. The results are summarized in Table I. The bands in the gas phase spectra are shifted 29–50  $\text{cm}^{-1}$  to lower energy of the values in the neon matrix, which is different from the hydrogenated chains, where blueshifts are the rule.<sup>12</sup> However, redshifts have been observed for some carbon anions.<sup>8</sup>

In Fig. 2 the  $0_0^0$  band is shown, recorded with 0.03  $\text{cm}^{-1}$  laser resolution (a). Several sharp lines appear, some of which are due to rotational transitions in the 0–0 and 1–1 vibrational bands of the  $d\ {}^3\Pi_g \leftarrow a\ {}^3\Pi_u$  electronic transition

<sup>a)</sup>Permanent address: I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany.

<sup>b)</sup>Electronic mail: maier@ubaclu.unibas.ch

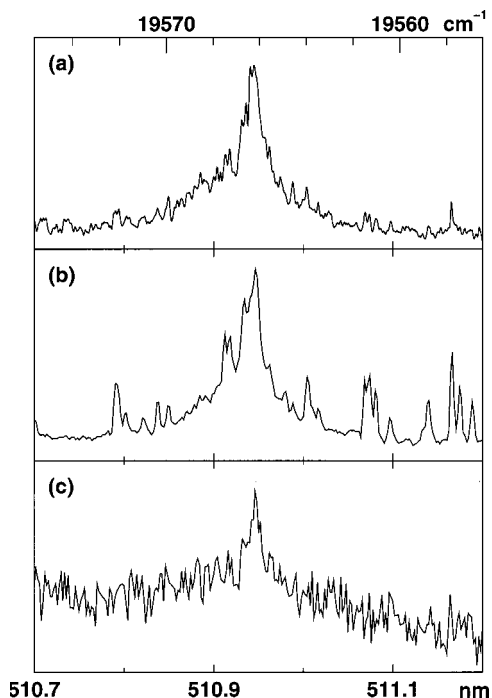


FIG. 1. The origin band of the  ${}^1\Pi_u \leftarrow X {}^1\Sigma_g^+$  electronic transition of  $C_5$  measured by cavity ring down spectroscopy with  $0.15 \text{ cm}^{-1}$  resolution in a supersonic slit nozzle plasma. The plasma is generated by discharge through 3% HCCH, 1%  $\text{CO}_2$  in Ne (a) and 0.2% DCCD in He (b) and by graphite laser vaporization (c). Absorption features originating from the  $C_2$  Swan system (see also Fig. 2) are more pronounced in (b), where a more diluted mixture was used.

of  $C_2$ . These are identified in trace (b), recorded under conditions that do not favor cluster formation (0.2% HCCH in He at low backing pressure). In the case of the  $2_0^1$  band (d) there is hardly any overlap by  $C_2$  lines. These transitions are marked by an asterisk in traces (a) and (d). The remaining structure in the  $0_0^0$  and  $2_0^1$  band is due to the  ${}^1\Pi_u \leftarrow X {}^1\Sigma_g^+$  band system of  $C_5$ . The apparent partial “rotational” structure is irregular and does not fit the pattern expected on the basis of the simulation shown in trace (c). The simulation is obtained with  $B''=0.085\ 313\ 3 \text{ cm}^{-1}$ ,<sup>23</sup>  $B'=0.0855 \text{ cm}^{-1}$ ,  $T_{00}=19\ 566.56 \text{ cm}^{-1}$ , a Gaussian linewidth of  $0.05 \text{ cm}^{-1}$  (a dashed line), and  $T_{\text{rot}} \approx 30 \text{ K}$ .<sup>11</sup> The observed irregular and broadened structure could be partially due to an overlapping sequence transition, but it is more likely that interactions with other electronic states are involved. Calculations on  $C_5$  predict several singlet and triplet states present below the

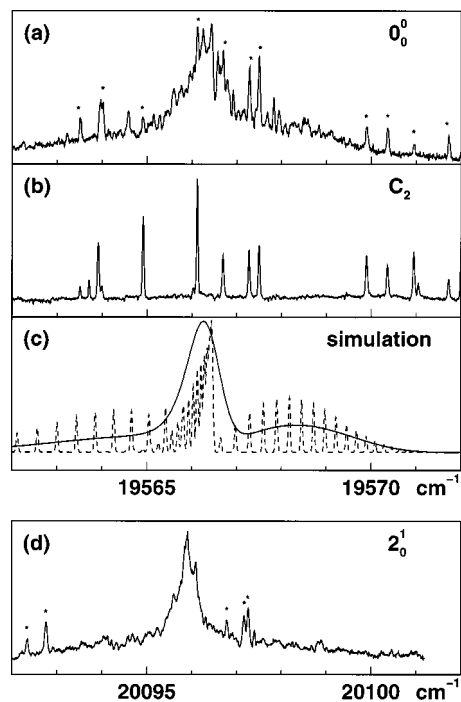


FIG. 2. High resolution spectrum ( $0.03 \text{ cm}^{-1}$ ) of the origin (a) and  $2_0^1$  band (d) of the  ${}^1\Pi_u \leftarrow X {}^1\Sigma_g^+$  electronic transition of  $C_5$ . The features marked with an asterisk are due to  $C_2$  transitions that are shown in (b) for the  $0_0^0$  band region. In (c) the simulated spectrum is shown for  $0.7 \text{ cm}^{-1}$  (the solid line) and  $0.05 \text{ cm}^{-1}$  (the dashed line) linewidth.

excited  ${}^1\Pi_u$  state,<sup>24</sup> which may give rise to the appearance of additional lines and offer an efficient relaxation pathway. One of the reasons why Douglas proposed that carbon chains should be considered as DIB carriers was the expected broadening resulting from intramolecular processes.<sup>4</sup> This is the first direct observation of such phenomenon for the bare neutral carbon chains.

A comparison to astronomical observations is of interest. The maxima of the measured bands (Table I) have been compared to the listing of diffuse interstellar bands.<sup>25</sup> Three of the observed bands ( $0_0^0$ ,  $7_0^2$ , and  $2_0^1$ ) overlap with DIBs, which are however too broad [full width at half-maximum (FWHM) over 1 nm] to match the narrower profiles of  $C_5$ . The FWHM of the strong  $Q$  branch does not exceed 0.05 nm. This means that if  $C_5$  is present in diffuse interstellar clouds, column densities are too small to be detectable via this transition. As the signal-to-noise ratio of the best DIB spectra of moderately reddened stars [ $E(B-V) \sim 1$ ] in this wavelength

TABLE I. Observed bands (maxima) of the electronic  ${}^1\Pi_u \leftarrow X {}^1\Sigma_g^+$  transition of  $C_5$  in the gas phase and in a neon matrix (Ref. 20).

Vibrational transition	Gas phase				Neon matrix		
	$\lambda$ (nm)	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$I^a$	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$I^a$
$0_0^0$	510.94(1)	19 566.3(2)	0	1.0	19 595(10)	0	1.0
$7_0^2$	503.81(1)	19 843.3(2)	277	0.4	19 885(10)	290	0.3
$2_0^1$	497.48(1)	20 095.9(2)	530	1.0	20 136(10)	541	1.1
	493.91(1)	20 241.0(4)	675	0.3	20 291(10)	696	0.3

<sup>a</sup>Relative intensity normalized on the origin band (error  $\sim 10\%$ ).

region can be as good as  $10^3$ , a  $0.5 \text{ \AA}$  broad 1% deep absorption feature is detectable. This corresponds to an equivalent width of  $0.005 \text{ \AA}$ . Assuming an oscillator strength  $f_{00} \approx 0.02$  for the  ${}^1\Pi_u \leftarrow X {}^1\Sigma_g^+$  transition by scaling the experimentally available value for C<sub>3</sub> ( $f_{00} \approx 0.016$ ),<sup>26</sup> a  $0.005 \text{ \AA}$  limit of equivalent width implies a C<sub>5</sub> column density  $\leq 10^{12} \text{ cm}^{-2}$ . This may be compared to an estimated value of  $4 \times 10^{12} \text{ cm}^{-2}$  for C<sub>3</sub> in a translucent cloud measured towards the star HD 147889.<sup>14</sup>

The current work presents the first electronic gas phase spectrum of a neutral bare carbon chain larger than C<sub>3</sub>. It is expected that the observation of electronic transitions of the longer bare carbon chains is within capability of the present experiment.

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