The $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic spectrum of linear C_4 in the gas phase

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The $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic absorption spectrum of linear C_4 has been detected in the gas phase. The origin and several vibronic transitions have been recorded by means of cavity ring down spectroscopy through a supersonic planar plasma. The origin band is found at $26\,384.9(2)$ cm^{-1} (~ 379 nm). A partly rotationally resolved origin band spectrum yields a value of $B_0' = 0.1570(5)$ cm^{-1} for the electronically excited $^3\Sigma_u^-$ state. © *2000 American Institute of Physics.* [S0021-9606(00)30422-0]

INTRODUCTION

Carbon chain radicals have been a topic of many spectroscopic studies in recent years (see Refs. 1–4 and references therein). This is partly motivated by their role in combustion processes and interstellar chemistry but these species are also of interest from a fundamental point of view. This is particularly the case for C_4 for which several theoretical studies have been reported that are summarized in Ref. 2. These predict that the closed shell rhombic structure and the linear cumulenic triplet structure have ground state energies that are nearly isoenergetic.[5,6] Both structures have been observed, the cyclic using Coulomb explosion imaging[7] and the linear by high resolution infrared spectroscopy.[8,9] In case of the chain structure, values are available for the ground state vibrational frequencies,[8–13] electron affinity,[10] and ionization potential.[14] In this paper the detection of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition in the gas phase is reported. The origin of this transition has been predicted between 408 and 455 nm by several *ab initio* calculations[15–17] but was found experimentally near 380 nm in the absorption spectrum of a 5 K neon matrix containing mass selected C_4.[18] In the same study also numerous transitions to vibrationally excited levels in the upper electronic state were assigned.

EXPERIMENT

The experimental method has been described in detail[19] and has been successfully used to study the gas phase spectra of a series of carbon chain radicals.[20] The conditions are basically identical to those described in Ref. 21 for the production of C_5; a supersonic planar plasma is generated by discharging a high-pressure gas pulse (30 Hz repetition rate, 1 ms pulse length, 10 bar backing pressure with a current of ≈ 80 mA at -700 V) of a 3% C_2H_2 or C_2D_2 and a 1% CO_2/Ne mixture in the throat of a 3 cm×300 μm multilayer slit nozzle geometry. This setup offers a nearly Doppler free environment and adiabatic cooling yields rotational temperatures around 20 K in the detection zone. The observation of a signal at the same wavelength both in a C_2H_2 and C_2D_2 mixture (also without CO_2, although weaker) unambiguously

identifies the carrier as a pure carbon cluster. As carbon rod vaporization is expected to lead to a poor C_4 production[22] laser ablation was not used. A standard cavity ring down spectrometer is used to detect the signals in direct absorption. Typically 45 ring down events are averaged at each wavelength before the digitized data are downloaded to a workstation. The spectra are calibrated via neon atomic lines that are recorded simultaneously in the jet expansion. The laser bandwidth is about 0.035 cm^{-1} using an étalon in the dye laser cavity.
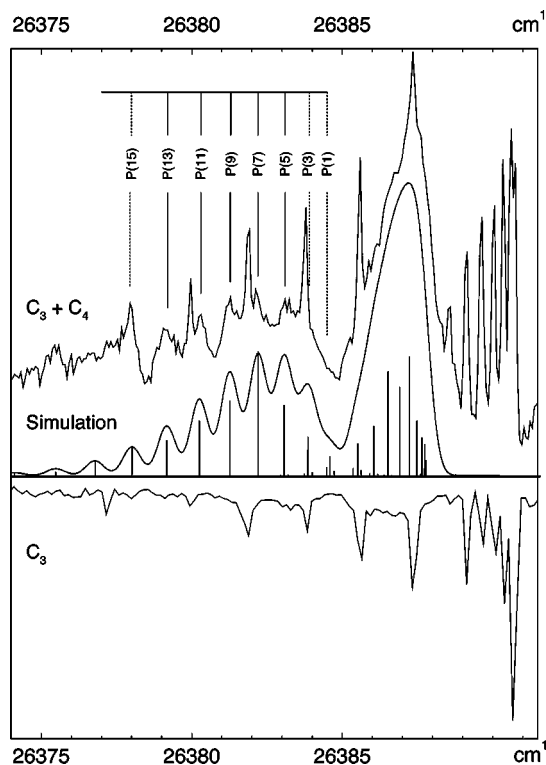

FIG. 1. The origin band of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition of C_4 is shown in the upper trace. The band system was measured with 0.035 cm^{-1} resolution by cavity ring down spectroscopy through a supersonic planar plasma by discharging 3% HCCH (or DCCD) and 1% CO_2 in Ne. The sharp features are due to a band of the $^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ electronic transition of C_3, seen in the lower trace (recorded with 0.15 cm^{-1} resolution) under conditions that do not favor C_4 production. In the middle part of the figure the simulated spectrum is shown, both lifetime broadened (0.7 cm^{-1}) and as a stick diagram.

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TABLE I. Assigned rotational transitions for the origin band in the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic spectrum of C_4. Values between brackets could not be observed directly. The accuracy is estimated to be of the order 0.2 cm^{-1}.

P (N)	ν (cm^{-1})
$P(1)$	(26 384.5)
$P(3)$	(26 383.9)
$P(5)$	26 383.1
$P(7)$	26 382.2
$P(9)$	26 381.3
$P(11)$	26 380.3
$P(13)$	26 379.2
$P(15)$	(26 378.0)

RESULTS

The upper trace of Fig. 1 shows the origin band of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition of C_4. The spectrum has spectral features consistent with a Σ–Σ transition of a linear molecule with P and R but without a Q branch. Rotationally resolved transitions in the P branch are hard to recognize at a first glance, as several lines are partly hidden by transitions belonging to a P branch of the C_3 species. The latter are shown in the lower trace of Fig. 1, recorded under conditions that do not favor C_4 production.

Each rotational level of C_4 is split into three fine structure levels characterized by the total angular momentum J ($J = N+1$, N and $N-1$, except for $N=0$ where $J=1$). This fine structure splitting is not observable under the present conditions, not even for the lowest J values. The P branch transitions are listed in Table I. A substantial decrease in the rotational B constant upon electronic excitation in combination with lifetime broadening prohibits the observation of the $P(1)$ transition and rotationally resolved transitions in the R branch, even though nuclear spin statistics determine that only odd values of N are allowed in the ground state of $^{12}C_4$. Consequently, it is not possible to link the electronic spectrum observed here to the available high resolution infrared data[9] via the combination differences. However, the spectrum is reasonably well reproduced, assuming a linear geometry in the electronically excited state and using the ground state constants available from the gas phase infrared spectrum ($B_0'' \approx 0.166\,111(7)$ cm^{-1} and $D_0'' = 0.282(14) \times 10^{-7}$ cm^{-1}).[9] The simulated spectrum is shown for

$B_0' = 0.1570(5)$ cm^{-1} and $T_{00} = 26\,384.9(2)$ cm^{-1} in Fig. 1 (middle trace), both lifetime broadened (0.7 cm^{-1}) and as a stick diagram. A decrease of 5.5% of the B constant upon electronic excitation is comparable to the 4.6% and 5.2% decrease observed for HC_4H^+[23] and C_4H,[24,25] respectively.

The observed linewidth must be due to a lifetime broadening, as the expected triplet splittings[26] and possible residual Doppler broadening are well below the resolving power of the laser. The presence of efficient internal relaxation pathways in carbon chains was proposed as a nondissociative broadening mechanism that might also account for the widths of diffuse interstellar absorption bands.[27] The approximately 50 ps lifetime of the excited $^3\Sigma_u^-$ electronic state of C_4 is comparable to that inferred for the upper state of C_5 from its $^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ electronic transition.[19]

Besides the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ origin band of C_4 a series of transitions to vibrationally excited levels in the upper state have been observed in a neon matrix;[18] two bands are of similar intensity as the origin band (2_0^1 and 1_0^2) and two bands are nearly twice as strong (1_0^1 and $1_0^1 2_0^1$). These bands have also been observed in the gas phase (Table II). The rotational contours are again visible, as shown in Fig. 2 for the band around 354.4 nm, but rotational structure could not be resolved as major parts of the 330–380 nm range are heavily overlapped by C_2 and C_3 absorption lines. Consequently, the accuracy with which the origin of the vibronic bands are determined (0.5–1 cm^{-1}) is not as good as usually obtained. For the same reason it is hard to unambiguously identify the weaker bands. The relative intensity of all vibronic bands is easily determined from the matrix absorption spectrum, but in the gas phase experiment this is more difficult, as different mirrors sets are necessary to cover the 50 nm wavelength range and production conditions during the respective measurements may vary. Qualitatively, however, the absorption strengths behave as one would expect from the matrix data (Table II).

C_4 may be of astrophysical relevance. Electronic transitions of the neutral pure carbon species C_2 and C_3 have been observed in diffuse and translucent interstellar clouds, respectively.[28] C_3 and C_5 have also been detected in circumstellar shells of carbon rich stars.[29] The present study may guide a search for linear C_4 in the diffuse interstellar medium. With the current setup it may also be possible to ob-

TABLE II. Observed band origin positions of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition of C_4 in the gas phase and in a neon matrix (Ref. 18).

Vibrational transition	Gas phase				Neon matrix		
	ν (cm^{-1})	λ (nm)	$\Delta\nu$ (cm^{-1})	I^{a}	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	I^{a}
0_0^0	26 384.9(2)	378.90	0	1.0	26 323(15)	0	1.00
2_0^1	27 254(1)$^{\text{b}}$	366.82	869	0.8	27 226(15)	903(20)	0.65
1_0^1	28 206(1)	354.44	1821	1.6	28 145(20)	1822(25)	1.75
$1_0^1 2_0^1$	29 060(1)$^{\text{c}}$	344.02	2675	2.2	28 986(20)	2663(25)	1.80
1_0^2	29 902(2)	334.34	3517	$\cdots$	29 860(20)	3537(25)	0.90

$^{\text{a}}$Relative intensity normalized on the origin band (error ~10% for matrix and ~25% for gas phase).
$^{\text{b}}$A second band of a pure carbon species is found at 27 275(1) cm^{-1}. Although in better agreement with the observed matrix shift (890 vs 869 cm^{-1} compared to 903 cm^{-1}) the intensity is far too small.
$^{\text{c}}$Position of maximum intensity. A very weak band of a pure carbon species is found near 29 018 cm^{-1}.

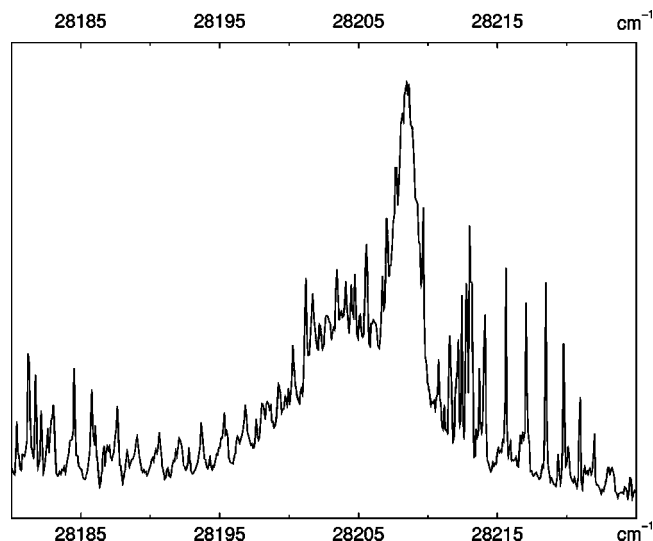J. Chem. Phys., Vol. 112, No. 22, 8 June 2000

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FIG. 2. The 1_0^1 band of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition of C_4. An unresolved P and R branch profile is clearly visible, but rotationally resolved transitions are not observed due to many overlapping C_2 and C_3 transitions.

serve the closed shell rhombic C_4, for which a strong electronic transition is calculated around 510 nm.[30]

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