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Sulfur terminated nanowires in the gas phase: laser spectroscopy and mass spectrometry

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Dedicated to Prof. Tilmann Märk on the occasion of his 60th birthday.

Abstract

The products of a CS_2-hydrocarbon discharge are elucidated through a combination of mass spectrometry and laser spectroscopy. Sulfur containing species are identified and their structures proposed using spectroscopic considerations. The resonant 2-color 2-photon ionization $A^2\Pi \leftarrow X^2\Pi$ spectrum of HC_6S is presented, confirming previous non-mass selective identification. The origin band of the $A^2\Pi \leftarrow X^2\Pi$ transitions of HC_8S and $HC_{10}S$ were measured at 14838.4(1) and 13333.7(5) cm^{-1} by cavity ringdown spectroscopy. The near linear relationship of absorption wavelength and chain length characterizes these species as molecular nanowires exhibiting cumulenic bonding. From these data $HC_{12}S$ is estimated to absorb at 820 ± 5 nm.

Keywords: Discharge; Optical spectroscopy; Carbon chains; Diffuse interstellar bands; Sulfur; Nanowires

1. Introduction

Sulfur-bearing conjugated carbon systems are of interest to many fields of scientific enquiry ranging from molecular electronics to astrophysics. As molecular electronic devices they are invoked due to the propensity of the sulfur terminal to bond to a gold surface [1]. Single sulfur-bearing conjugated molecules have been placed between gold electrodes with voltages applied between them, thereby allowing the measurement of current passing through a single molecule [2]. The current–voltage characteristics observed depends critically upon the electronic structure of the bridging sulfur-bearing conjugated carbon system [3].

It is known that sulfur plays an important part in the chemistry of the interstellar medium [4]. Sulfur-bearing carbon chains such as C_3S and C_5S have been discovered in space by rotational spectroscopy [5–7]. Sulfur heteroatoms terminating carbon chains cause strong polarization of the π-electron cloud and increases the oscillator strength of its electronic transitions. As such, despite the lower abundance of sulfur in the interstellar medium as compared to carbon, the sulfur terminated carbon chains can absorb strongly and may be considered as candidate carriers of the diffuse interstellar bands. Confirmation as carriers of diffuse interstellar bands can only come from a direct comparison with gas-phase optical laboratory spectra. As sulfur-bearing carbon chains such as C_nS and HC_nS are radicals, they must be produced as transient species. This is usually performed with a sulfur-seeded hydrocarbon discharge.

Such discharges have been utilized to produce laser-induced fluorescence spectra of the transient species $HC_{2n}S$ ($n = 1$–3) and the $SCCS^-$ anion [8–11], and pure rotational spectra of HC_nS ($n = 2$–8) [12,13] and C_nS ($n = 4$–9) [14]. Despite the importance of this discharge system for the production of sulfur-bearing species relevant to astrophysics, it has never been studied by a mass-selective technique.

The paper is arranged as follows. The CS_2/C_4H_2 discharge is analyzed by time-of-flight (TOF) mass spectrometry. The sulfur-bearing species are identified and structures are proposed. Mass-selective resonant 2-colour 2-photon ionization (R2C2PI) spectroscopy is used to confirm the previous assignment of the optical spectrum of HC_6S by laser-induced fluorescence spectroscopy [10]. The origin bands of HC_8S and $HC_{10}S$ and their deuterated analogs are presented for the first time, measured by cavity ringdown spectroscopy (CRDS). The results obtained by various techniques are

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combined to provide a diagnosis of the chemistry taking place in the CS_2/C_4H_2 discharge.

2. Experiment

2.1. R2C2PI TOF spectroscopy

The R2C2PI TOF experimental set-up has been described elsewhere [15]. It consisted of a molecular beam coupled to a linear TOF mass analyzer. The source used to produce sulfur-bearing carbon chains was a pulsed valve coupled to an electric discharge. A gas mixture pulse of 0.5% of butadiyne (HCCCCH) in Ar (backing pressure 8 bar) was passed through an ice-cooled reservoir of CS_2 and subsequently expanded through the ceramic body of the source. A high voltage pulse (600–900 V) from a home-built pulse generator was applied between the electrodes placed either side of the ceramic spacer. The emerging beam entered the ionization region through a 2 mm skimmer. The neutral molecules were then ionized and the ions extracted in a two-stage acceleration setup towards a multichannel plate detector. The signal from the detector was fed into an oscilloscope after pre-amplification and transferred to a computer.

R2C2PI spectra were recorded in the near UV and visible range. Excitation photons in the UV range came from the frequency doubled output of a dye laser (bandwidth $\sim 0.1\,\mathrm{cm}^{-1}$) pumped by the second harmonic of a Nd:YAG laser. Visible photons were produced by an excimer pumped dye laser. The ionizing photons at 157 nm were produced by an F_2 excimer laser with the energy of a few mJ/pulse. Photons of wavelength 193 nm were produced by an ArF excimer laser with pulse energies of 100 mJ. The excitation laser was anticollinear while the excimer laser was perpendicular to the molecular beam. Since the laser beams were unfocussed, multiphoton transitions were not expected.

2.2. CRD spectroscopy

The experiment is composed of a cavity ringdown (CRD) spectrometer sampling a supersonic planar plasma. The plasma was generated by a discharge through a gas pulse (−600 V, 30 Hz repetition rate) of a premixed precursor gas passing through a $3\,\mathrm{cm} \times 300\,\mu\mathrm{m}$ multilayer slit nozzle (backing pressure 10 bar). For production of HC_8S (DC_8S) a 0.5% C_2H_2 (and/or C_2D_2) with 0.1% CS_2 mixture in argon was used while for production of $HC_{10}S$ ($DC_{10}S$), C_2H_2 was substituted by 0.4% C_4H_2 (and/or C_4D_2). Rotational temperatures of the order of 20–40 K were routinely achieved. The nozzle was mounted in an optical cavity where the expansion was intersected approximately 2 mm downstream by the pulsed beam of a tunable dye laser (resolution $0.15\,\mathrm{cm}^{-1}$). The light leaking out of the cavity was detected with a photodiode, the resulting ringdown event being used as input for standard ringdown analysis [16]. The spectra were recorded by determining an averaged ringdown time as a function of the laser frequency, calibrated by a wavemeter.

3. Ab initio calculations

Quantum chemical calculations were performed using the GAMESS computational package [17]. The basis set employed for all calculations was the double-zeta basis of Dunning and Hay [18]. Ground state equilibrium geometries of HC_nS ($n = 2$–6) were calculated at the multi-configuration quasi-degenerate perturbation theory (MCQDPT) level of theory [19] with a minimal self-consistent field (SCF) reference wavefunction. Single point calculations for the neutral HC_nS species and their ions were then performed by MCQDPT using SCF and multi-configuration self-consistent field (MCSCF) reference wavefunctions. The latter calculations were performed with a complete active space comprising six orbitals with five electrons for $n = 3$, 5 and seven electrons for $n = 2$, 4, 6. Estimates of the vertical ionization potentials (IPs) of these species were made by taking the difference between the energy of the neutral and ionic species at the same level of theory.

4. Results and discussion

4.1. Mass spectrometry

Time-of-flight mass spectra recorded at ionization wavelengths of 157 and 193 nm are presented in Fig. 1. The 57 nm spectrum exhibits many more peaks than the 193 nm spectrum. This is a reflection of the number of species produced in the discharge for which the IP is lower than the photon energy. While the energy of a 193 nm photon is quite low (6.4 eV), it is sufficient to ionize the $C_{2n+1}H_3$

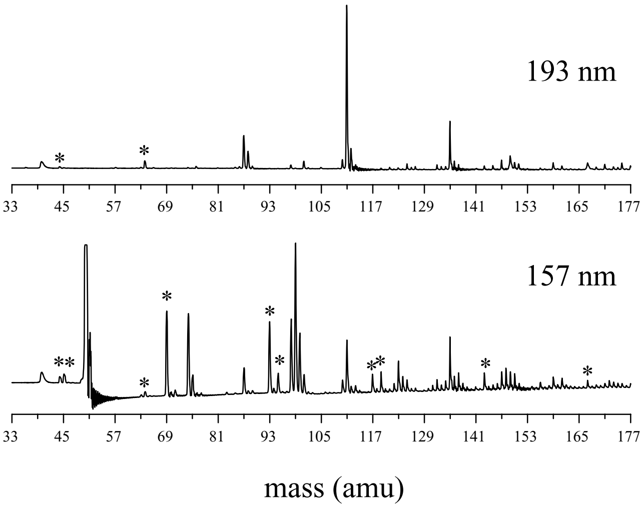

Fig. 1. Typical mass spectra from a CS_2/C_4H_2 discharge at two ionization wavelengths. Peaks determined to be sulfur-bearing are marked with ‘*’

Table 1
Selected mass peaks observed in the $CS_2/C_4H_2/Ar$ discharge irradiated with either 193 or 157 nm

Mass	Molecular formula
40	Ar
44	CS
45	HCS
50	HCCCCH
64	S_2
69	**HCCCS**
74	HC_6H
87	C_7H_3
93	**HCCCCCS**
95	**H_2CCCCCSH**
111	C_9H_3
117	**HCCCCCCCS**
119	**H_2CCCCCCCSH**
135	$C_{11}H_3$
143	**H_2CCCCCCCCCSH**
167	**H_2CCCCCCCCCCCSH**

Sulfur-bearing carbon chains are emboldened. The formulae ascribed to masses 95, 119, 143 and 167 are tentative and are discussed in the text.

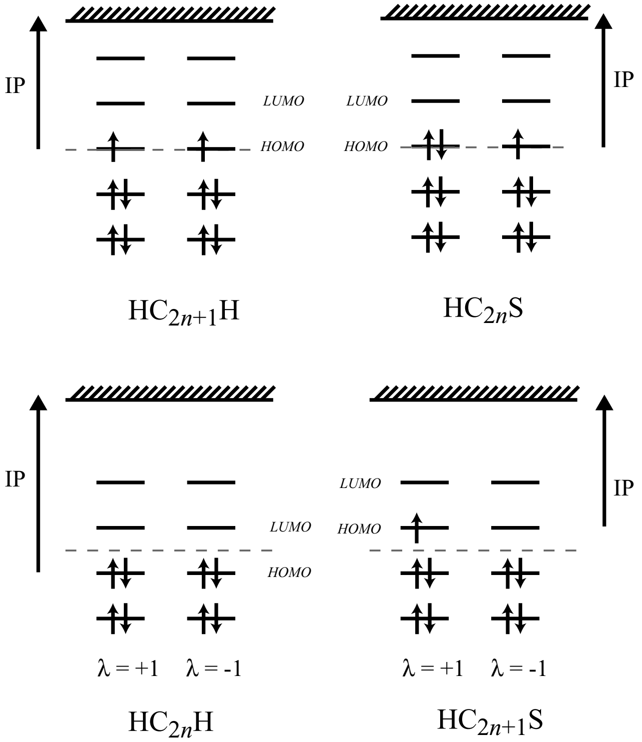

Fig. 2. A cartoon description of the electronic ground states of HC_nH and HC_nS. Indicated is the IP and λ, the projection of orbital angular momentum onto the molecular axis. It is seen that the $HC_{2n+1}S$ species possess electrons occupying orbitals above the Fermi level (dotted line) of the corresponding all-carbon π-system ($HC_{2n}H$). This accounts for these species' low IPs.

series [20] which dominates the mass spectrum. The structure of these species has not been unambiguously identified yet it is probable that they comprise a three-membered ring which possesses aromatic stability in its ionic form. While the intensity of the 193 nm radiation was two orders of magnitude larger than that of the 157 nm beam, the large peaks in the mass spectrum are not believed to arise from two-photon ionization. Some of the smaller peaks (certainly mass 40, Ar^+) derive from ionization of molecules trapped in long lived metastable states.

Variation of the concentration of CS_2 in the discharge made it possible to determine the sulfur containing species. Assignments of prominent peaks to molecular formulae are given in Table 1. On increasing the ionization photon energy from 6.4 eV (193 nm) to 7.9 eV (157 nm), many more species are observed. Two notable series are the $HC_{2n+1}S$ ($n = 1$–3) chains and another 14 mass units heavier.

The appearance of the $HC_{2n+1}S$ series as strong peaks under irradiation at 7.9 eV suggests quite low IPs. This is predicted by ab initio calculations and may be justified by invoking simple Hückel considerations. The terminal sulfur atom is capable of taking part in the π-bonding network. As such, after taking account of one electron for the sigma-bond to its neighbouring carbon atom, and two electrons for a lone pair, this leaves three electrons to allocate to the delocalized π-system. Because the π-system is more than half filled for odd numbers of carbon atoms, the IP will be low (see Fig. 2). However, since the peaks are not observed in the 193 nm mass spectrum, the IPs of these chains must lie above 6.4 eV. This situation does not arise for the $HC_{2n}S$ chains. Since HC_6S was not observed strongly in the spectrum presented in Fig. 1, it is supposed that the IP of this species lies above 7.9 eV. Since the excitation spectrum of HC_6S was measured by R2C2PI spectroscopy utilizing 193 nm as the ionizing laser, its IP must lie below 8.5 eV, as discussed below. The results of quantum chemical calculations are presented in Fig. 3. Overall, the calculated values seem low, yet all levels of theory are in agreement with respect to the odd–even alternation.

The second series, 14 mass units heavier, commences at 95 a.m.u., which would correspond to a molecule of formula C_5H_3S. The addition of CH_2 to the HC_nS chains may result in methyl-terminated chains. It has been shown that

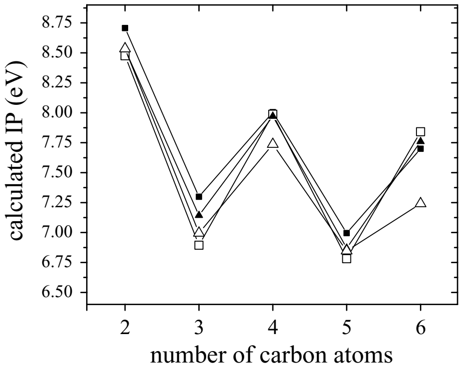

Fig. 3. The calculated vertical IPs for the HC_nS ($n = 2$–6) carbon chains. MCQDPT values are given as open symbols and those of MCSCF as filled ones. The SCF (squares) and (5, 7/6) MCSCF reference wavefunctions (triangles) both indicate odd–even alternation of IPs as justified in the text.

methyl substitution for a hydrogen is prevalent in a hydrocarbon discharge [21]. However, in this case the pattern of substitution seems unlikely. While the peak corresponding to C_7H_3S could be caused by CH_3C_6S, this species should have an IP and excitation spectrum similar to the unsubstituted species, HC_6S. As will be shown below, such a spectrum is not observed. In order to have low IPs, similar to the $HC_{2n+1}S$ series, the π-system must contain an even number of atoms (including the −S moiety). Moving one hydrogen from the methyl group of $CH_3C_{2n}S$ to the sulfur terminal, results in species of formula $H_2C_{2n+1}SH$, which will behave in a similar way to the $HC_{2n+1}S$ series with respect to IP. The structurally similar cumulenethiones H_2C_nS ($n = 4$–7) have been observed by rotational spectroscopy [12], but were not observed by mass spectrometry of the discharge source.

In addition to the species discussed above, numerous others were observed. Those easily identifiable by their R2C2PI spectra included CS, HCS, S_2, CCS and CS_2.

4.2. Ionization spectroscopy

The mass spectrometry detailed above was used as a tool to tune the discharge conditions to produce desired carbon chain species. Fig. 4 shows the origin band and one hot band of HC_6S. The mass-selective measurement of this band confirms the observation of this species by laser-induced fluorescence [10]. One new band of this molecule was obtained 782.9 cm^{-1} to lower energies than the origin. The C=S stretch is observed to be around 500 cm^{-1} in these $HC_{2n}S$ species [8–10], yet as high as 863 cm^{-1} for CCS. Since the C=S stretches in the ground states of similar molecules lie much lower than the 782.9 cm^{-1} energy difference observed here, the band is assigned as a hotband starting from double excitation of a bending mode in the ground state.

The spectrum of HC_6S was obtained readily utilizing 193 nm as the ionizing wavelength. This places the IP of HC_6S below 8.5 eV. Despite 157 nm photons being energetic enough to ionize electronically excited HC_6S, the intensity of this wavelength was about two orders of magnitude weaker than that at 193 nm and in this case not intense enough to produce observable signal. (The spectrum of HC_6S utilizing 157 nm as the ionizing wavelength has been subsequently observed in our laboratory.)

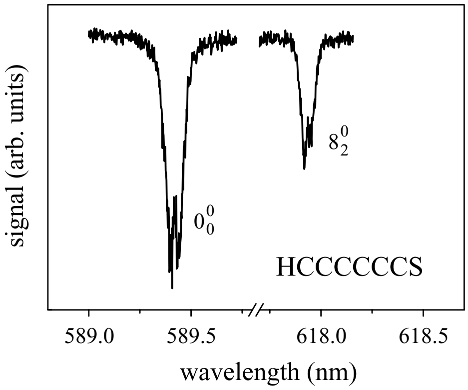

Fig. 4. Bands of HC_6S measured by R2C2PI spectroscopy. The mass-selective measurement confirms the identification by LIF spectroscopy (Ref. [10]). The hotband 782.9 cm^{-1} to the red is assigned to doubly excited bending in the ground state (8^0_2)

A search for HC_8S using R2C2PI spectroscopy was unsuccessful. Utilization of 193 nm as the ionizing wavelength while exciting HC_8S around 677 nm produces a combined photon energy of 8.26 eV. It is possible that the IP of HC_8S lies above this value, yet it should lie below 8.5 eV (the upper limit for HC_6S) assuming the normal trend of IP to decrease with chain length. The non-observation is suggested to be caused by a short lifetime (≈ps) in the upper state. Observation of HC_8S was also unsuccessful using 157 nm, for the reasons outlined above.

Also observed by 2-colour and 1-colour ionization spectroscopy in this discharge were the S_2, CS, CCS and C_3 molecules. The $E^3\Sigma^- \leftarrow X^3\Sigma^-$ spectrum of CCS was measured for the first time in the gas phase, following the identification of the band system in a neon matrix [22]. However, rotational profiles were not obtained, and thus a test of the predicted bond lengths was not possible.

Since the peak in the mass spectrum for mass 119 was observed to be strong, it is assumed that the molecule responsible for this peak is abundant in the discharge. Were this molecule to be a methyl-substituted version of HC_6S, namely CH_3C_6S, then one would expect to have observed a R2C2PI spectrum under the same conditions as that for which HC_6S was observed. The negative result and observation of low IPs for the $H_3C_{2n+1}S$ series suggests an alternative identity for this series as discussed in Section 4.1.

4.3. Cavity ringdown spectroscopy

Fig. 5 shows the measured origin bands of HC_8S and DC_8S measured by CRDS. The origin position of HC_8S,

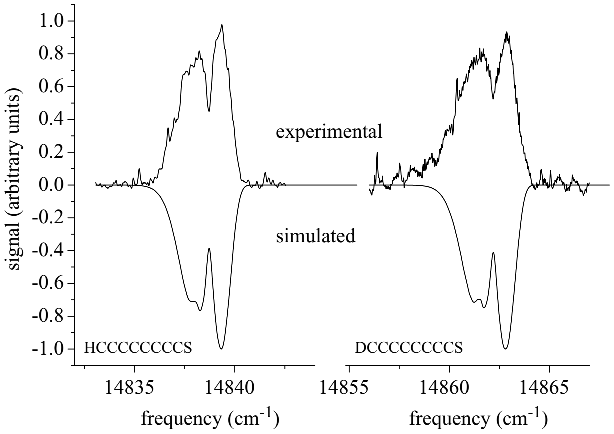

Fig. 5. The origin band of HC_8S (left) and DC_8S (right) measured by CRDS. The origin of HC_8S lies 80 cm^{-1} to the blue of the prediction in Ref. [5], based on a linear relationship of the absorption wavelength and chain length. Simulations were performed using the spectroscopic constants listed in Table 2.

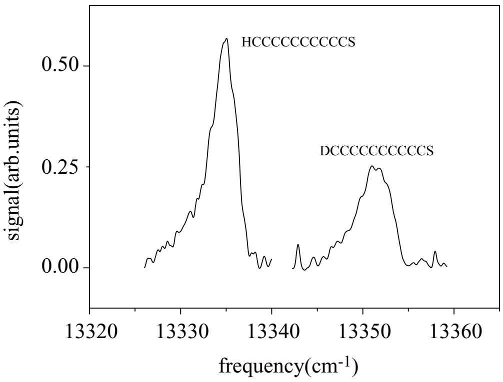

Fig. 6. Origin bands of $HC_{10}S$ (left) and $DC_{10}S$ (right) measured by CRDS. From the broadening of the bands the excited state lifetime is estimated to be about 2.6 ps.

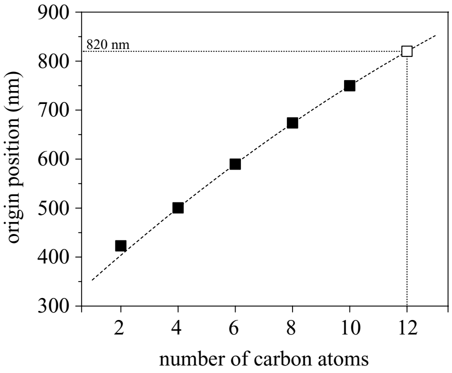

Fig. 7. A plot of the origin band wavelength of the $HC_{2n}S$ series as a function of the number of carbon atoms in the chain, $2n$. The relationship is remarkably linear, a reflection of the cumulenic bonding in these systems. A quadratic fit to the points measured for $n = 2$–5 yields an estimate for the absorption position of $HC_{12}S$ of 820 nm.

14838.4 cm^{-1}, is only 80 cm^{-1} to the blue of that predicted by a linear relationship between chain length and origin wavelength, extrapolated from the smaller species, HC_2S, HC_4S, and HC_6S [9,10]. The slight deviation from linearity is continued for $HC_{10}S$ and its deuterated analog, $DC_{10}S$. The broad spectra of these species are shown in Fig. 6. The origin positions of $HC_{10}S$ and $DC_{10}S$ cannot be estimated better than the laser resolution (0.15 cm^{-1}) due to the severe lifetime broadening. Spectroscopic constants for HC_8S, DC_8S, $HC_{10}S$ and $DC_{10}S$ are given in Table 2.

The strongly linear relationship between absorption wavelength and chain size is a reflection of the cumulenic bonding structure in the HC_nS species induced by the carbon–sulfur double bond. The bonding pattern was confirmed by the quantum chemical calculations described above. This relationship is also seen in the C_nH^- anions [23], where one end of the chain exhibits cumulenic bonding which merges smoothly to acetylenic character on moving to the terminal hydrogen. It is this acetylenic character, induced at the hydrogen terminal, which explains (at the Hückel level of theory) the deviation from linearity. It has been shown that for the long carbon chains, $HC_{2n}H$, the relationship between chain length and absorption wavelength is strongly non-linear [15]. As the near-linear relationship is expected to continue, a prediction can be made for the origin position of $HC_{12}S$. Based on the present data (making a small correction due to non-linearity), this species is expected to absorb at 820 ± 5 nm. (See Fig. 7.)

Table 2
The origins and the effective rotational constants (in cm^{-1}) of the vibronic bands of the HC_8S and $HC_{10}S$ radicals, and their deuterated analogs

	T_0	B''	B'	ΔA_{SO}
HC_8S	14838.4(1)	0.00958[a]	0.00954(2)[b]	0.7
DC_8S	14861.9(1)	0.00938(2)[c]	0.00935(3)[b]	0.7
$HC_{10}S$	13333.7(5)	0.00551(1)[d]	0.00542(5)[b]	2.5
$DC_{10}S$	13350.8(5)	0.00541(1)[c,d]	0.00535(5)[b]	2.5

Spin orbit constants are in the vicinity of 25 cm^{-1}. Only the change in A_{SO} could be determined accurately by the fitting procedure.

[a] Previously determined by microwave spectroscopy [12].

[b] Rotational constants in the excited state were extrapolated using the rotational constant ratio B''/B' of HC_6S and HC_4S. Reported errors were estimated during the fitting procedure.

[c] The rotational constants of the deuterated species in the ground state were calculated according to the assumption that the structure of deuterated species is unchanged upon isotopic substitution.

[d] The rotational constant of $HC_{10}S$ in the ground state was estimated under consideration of increasing chain length.

The shift in origin band position upon deuterium substitution is caused by the difference in zero-point energies in the ground and excited states. This is 23 cm^{-1} to higher energies for HC_8S and 17 cm^{-1} for $HC_{10}S$. This compares with 35 cm^{-1} for HC_6S and 54 cm^{-1} for HC_4S. The decreasing deuterium shift upon increasing the chain size reflects the decreasing effect that the electronic excitation has on the vibrational modes involving motion of the hydrogen (deuterium) moiety. With this in mind, it is expected that the origin band position of $DC_{12}S$ will lie about 12 cm^{-1} to the blue of the $HC_{12}S$ band position.

It has been noted that the excited state lifetimes of the $HC_{2n}S$ series decrease with increasing chain length. Laser-induced fluorescence work has estimated the lifetimes of HC_4S and HC_6S to be 30 ns and 270 ps, respectively [9,10]. The lifetime of HC_8S is thus expected to be shorter still. Due to lack of resolution, the lifetime could not be estimated from the spectrum displayed in Fig. 5. The line width used in the simulated spectra was that of the laser resolution used, 0.15 cm^{-1}. If the lifetime broadening is no more than this order of magnitude, a conservative lower limit for the lifetime can be made of 70 ps. From spectral simulation, the lifetime of the $A^2\Pi$ excited state of $HC_{10}S$ is estimated to be 2.6 ps. Short excited state lifetimes have implications for selecting the energy of the second photon when measuring R2C2PI spectra.

5. Conclusions

By time-of-flight mass spectrometry it was found that a sulfur-seeded hydrocarbon discharge produces a range of hydrogen and sulfur-bearing carbon chains, and that these species dominate the discharge chemistry. This is in accord with previous detection of sulfur-bearing chains as products of CS_2/hydrocarbon discharges. The dominant series appearing in the mass spectrum under irradiation by 157 nm light are the $HC_{2n+1}S$ series and another 14 a.m.u. higher for which the identity is suggested to be $H_2C_{2n+1}SH$. The low IPs for the $HC_{2n+1}S$ series were predicted semi-quantitatively by quantum chemical calculations. The production of the even chains $HC_{2n}S$ was confirmed by R2C2PI spectroscopy and cavity ringdown spectroscopy. The spectrum of HC_8S was measured for the first time and was found to lie within 80 cm^{-1} of the prediction according to an extrapolation from smaller members of the same series [8–10]. The extremely broad origin band of $HC_{10}S$ was measured for the first time and confirmed the slight deviation from linearity of the relationship between chain size and absorption position. This measurement provided an updated estimate for the position of the $HC_{12}S$ origin band, which is expected to be found near 820 nm. The near linear relationship between the absorption wavelength and the length of the carbon chain is indicative of cumulenic bonding. There is no evidence for a bandgap developing for long $HCC\cdots CCS$ chains and thus they are expected to exhibit conducting properties if employed as molecular wires. None of the spectra of the $HC_{2n}S$ chains match those of the DIBs. The predicted position of the origin band of $HC_{12}S$ does not lie nearby any DIBs and thus these species can be ruled out as carriers thereof.

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References

[1] M.G. Samant, C.A. Brown, J.G. Gordon, Langmuir 8 (1992) 1615.
[2] M.A. Reed, C. Zhou, C.J. Muller, T.P Burgin, J.M. Tour, Science 278 (1997) 252.
[3] V. Mujica, A. Nitzan, S. Datta, M.A. Ratner, C.P. Kubiak, J. Phys. Chem. B 107 (2003) 91.
[4] R. Lucas, H.S. Liszt, Astron. Astrophys. 384 (2002) 1054.
[5] T.J. Millar, J.R. Flores, A.J. Markwick, Mon. Not. R. Astr. Soc. 327 (2001) 1173.
[6] M.B. Bell, L.W. Avery, P.A. Feldman, Astrophys. J. 417 (1993) L37.
[7] J. Cernicharo, M. Guelin, H. Hein, C. Kahane, Astron. Atrophys. 181 (1987) L9.
[8] S.L.N.G. Krishnamachari, T.V. Venkitachalam, Chem. Phys. Lett. 55 (1978) 116;
S.L.N.G. Krishnamachari, D.A. Ramsay, Faraday Discuss. Chem. Soc. 71 (1981) 205.
[9] M. Nakajima, Y. Sumiyoshi, Y. Endo, Chem. Phys. Lett. 351 (2002) 359.
[10] M. Nakajima, Y. Sumiyoshi, Y. Endo, Chem. Phys. Lett. 355 (2002) 116.
[11] M. Nakajima, . Yoneda, Y. Sumiyoshi, T. Nagata, Y. Endo, J. Chem. Phys. 119 (2003) 7805.
[12] V.D. Gordon, M.C. McCarthy, A.J. Apponi, P. Thaddeus, Astrophys. J. Supp. Ser. 138 (2002) 297.
[13] Y. Hirahara, Y. Oshima, Y. Endo, J. Chem. Phys. 101 (1994) 7342.
[14] V.D. Gordon, M.C. McCarthy, A.J. Apponi, P. Thaddeus, Astrophys. J. Supp. Ser. 134 (2001) 311.
[15] T. Pino, H. Ding, F. Güthe, J.P. Maier, J. Chem. Phys. 114 (2001) 2208.
[16] A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum. 59 (1988) 2544.
[17] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
[18] T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), Methods of Electronic Structure Theory, Plenum Press, New York, 1977, Chapter 1, p. 1.
[19] H. Nakano, J. Chem. Phys. 99 (1993) 7983.
[20] T.W. Schmidt, A.E. Boguslavskiy, H. Ding, T. Pino, J.P. Maier, Int. J. Mass. Spectrom. 248 (2003) 647.
[21] T.W. Schmidt, H. Ding, A.E. Boguslavskiy, T. Pino, J.P. Maier, J. Phys. Chem. A 107 (2003) 6550.
[22] E. Riaplov, M. Wyss, J.P. Maier, D. Panten, G. Chambaud, P. Rosmus, J. Fabian, J. Mol. Spectrosc. 222 (1) (2003) 15.
[23] D.A. Kirkwood, M. Tulej, M.V. Pachkov, M. Schnaiter, F.Güthe, M. Grutter, M. Wyss, J.P. Maier, G. Fischer, J. Chem. Phys. 111 (1999) 9280.