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# Gas-Phase Electronic Absorption Spectra of Deuterated Linear Seven-Carbon Radicals

M. A. HADDAD, D. ZHAO, and W. UBACHS

*Department of Physics and Astronomy, LaserLaB, VU University, De Boelelaan, Amsterdam, the Netherlands*

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Rotationally resolved gas-phase absorption spectra of partially and fully deuterated linear seven-carbon chain radicals are presented in this article. The carbon-based molecules are generated in a supersonically expanding planar plasma by discharging a gas mixture of acetylene and deuterium-enriched acetylene in helium and argon. Spectra are recorded in direct absorption using cavity ring-down spectroscopy. The rotational analyses of the present experimental spectra allow to determine both ground and excited state rotational constants, as well as the upper state band origins of the two deuterated species.

**Keywords:** carbon chain radicals, cavity ring-down spectroscopy, electronic spectroscopy, $HC_7D$ and $DC_7D$

## Introduction

Carbon is a major player in the chemistry of the dilute gas in clouds between the stars, because of its abundance and its ability to form complex species. While 75% of the molecules detected in interstellar space are carbon-bearing, they are also key elements in the evolution of prebiotic molecules.[1] Highly unsaturated carbon chain radicals have been identified in dark interstellar clouds following radio-astronomical observations.[2,3] Centro-symmetric chains such as $NC_nN^{(+)}$ and $HC_nH^{(+)}$ are expected to exist in the interstellar medium as well but are radio-silent given their lack of a permanent dipole moment.[4] These chains are only detectable via low-lying bending modes, typically in the sub-millimeter region, or via infrared spectra of vibrational bands.[5–7] Optical transitions offer another alternative, particularly towards diffuse and translucent clouds, where electronic transitions of carbon chains have been associated with diffuse interstellar band features.[8]

The electronic $\tilde{A}^3\Sigma_u^- - \tilde{X}^3\Sigma_g^-$ transitions of the odd-polyyne $HC_{2n+1}H$ series have been investigated experimentally in laboratory studies. Their electronic absorption spectra have been recorded in 5 K neon matrices, providing origin band transitions as well as transitions to vibrationally excited states in the $\tilde{A}^3\Sigma_u^-$ state.[9] Guided by these data, the gas phase spectra have been recorded for $HC_{2n+1}H$ (n=2–6), using different spectroscopic techniques such as two-color two-photon-ionization[10] and cavity ring-down spectroscopy.[11,12] The latter technique has resulted in rovibronically unresolved spectra of $HC_{2n+1}H$ species and their corresponding partially or fully deuterated isotopologues using a pinhole plasma expansion. In more recent work[13], partially resolved spectra for $HC_7H$ have been reported, using a planar plasma source with a reduced Doppler broadening in combination with an improved laser bandwidth. The present study utilizes the same method and extends results to $HC_7D$ and $DC_7D$, whose band origin positions have been reported previously,[12] but a rotational analysis is lacking so far.

The aim of the present study is to enlarge the spectroscopic database for carbon-based radicals to be used as a reference for the identification of species in dilute and optically transparent interstellar clouds.

## Experimental

The gas-phase electronic spectra of linear $HC_7D$ and $DC_7D$ are recorded by pulsed cavity ring-down spectroscopy. The experimental setup, shown in Fig. 1, has been documented in Refs.[13–15], and here some essential details are described. The partially and fully deuterated carbon chain radicals are generated by discharging a pulsed gas mixture (0.15% $C_2D_2$ or ~0.35% $C_2H_2 + 0.15\%$ $C_2D_2$ in a 7:3 He:Ar mixture) of 1 ms duration in the throat of a slit discharge nozzle. It is found in the present experiment that, with the same discharge condition, the carbon chain production efficiency can be increased by a factor of 3–4 by adding argon to the expanding gas mixture. This may be due to the fact that argon decreases the overall expanding velocity and consequently results in more collisions in the discharge area. The gas is expanded with a backing pressure of about 10 bar through a long and narrow (3 cm × 300 μm) slit that is positioned parallel to the laser beam and offset by a few millimeters with respect to

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Address correspondence to W. Ubachs, Department of Physics and Astronomy, LaserLaB, VU University, De Boelelaan 1081, NL 1081 HV, Amsterdam, the Netherlands. E-mail: w.m.g.ubachs@vu.nl

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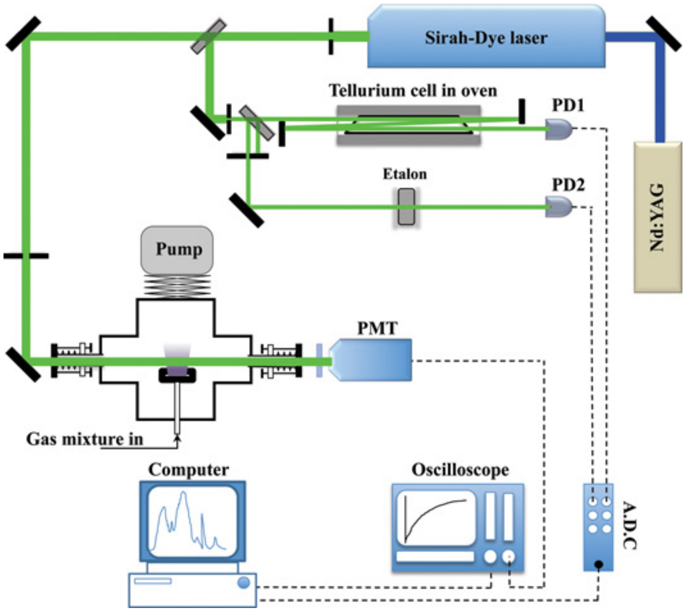

**Fig. 1.** The experimental setup.

the optical axis of a high finesse cavity of length 58 cm, consisting of two high reflectivity mirrors. Tunable light with a bandwidth of ~0.035 cm$^{-1}$ is generated by a tripled Nd:YAG laser (355 nm, 8 Hz) pumped dye laser (Sirah, Cobra-Stretch), operated in a second-order grating configuration, and spatially filtered before it is focused into the optical cavity. Light leaking out of the cavity is detected by a photo-multiplier tube, and the ring-down signals are converted into an optical absorption spectrum.[16] The laser frequency is accurately calibrated by simultaneously recording a 650°C tellurium vapor absorption spectrum and linearized using an etalon with a free spectral range of 0.7 cm$^{-1}$. This yields an absolute laser frequency accuracy of 0.02 cm$^{-1}$.

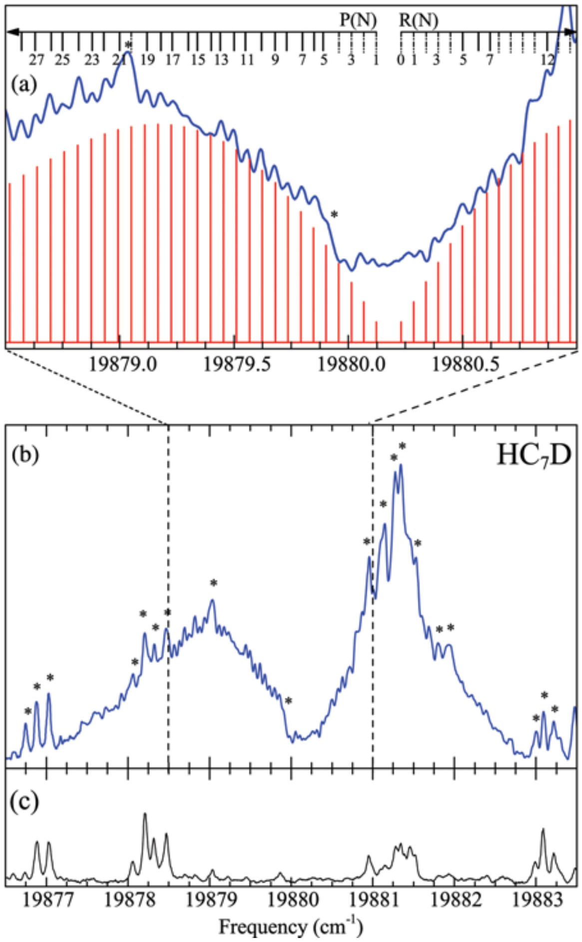

**Fig. 2.** (a) The expanded spectrum of the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ electronic transition of $HC_7D$ (upper trace) in the band origin region compared with a simulated stick diagram using an effective $^1\Sigma - {}^1\Sigma$ Hamiltonian. The full spectrum is shown in panel (b). Peaks due to overlapping spectra originating from other species are marked by an asterisk and shown in panel (c) for expansion conditions not in favor of carbon chain formation.

## Results and Discussion

### *$HC_7D$*

Panel (b) of Fig. 2 shows the experimental spectrum of the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ electronic origin band transition of $HC_7D$. The observed band, recorded at a S/N of ~25, exhibits a partially resolved rotational structure that is spectrally polluted by overlapping narrow features due to other (smaller) hydrocarbon compounds. This is illustrated in panel (c) for expansion conditions not in favor of carbon chain formation – lower backing pressures and lower discharge current – from which the polluting peaks can be easily discriminated. The spacing between individual rotational transitions in P- and R-branches of the asymmetric $HC_7D$ molecule is not similar to the symmetric $HC_7H$ (or $DC_7D$) species, as spin-statistics do not apply; i.e., the spacing between subsequent rotational transitions is approximately $2B$, rather than $4B$. A zoom-in view of the spectrum (panel (a) of Fig. 2) illustrates that many of the individual transitions indeed are resolved.

For a $^3\Sigma$ electronic state, due to spin-rotational interactions, rotational levels are split into triplet fine structure levels: $F_1$ for $N = J - 1$, $F_2$ for $N = J$, and $F_3$ for $N = J + 1$. In the general case the energy eigenvalues of triplet fine structure levels of the same $N$ are close to each other and $N$ is a good quantum number for assigning rotational transitions. Under this assumption the rotational analysis of the spectrum can be performed by employing an effective $^1\Sigma$–$^1\Sigma$ transition, with the assumption that spin-rotation and spin-spin interaction are not affecting the overall pattern too much. Under this assumption of spin-interactions set to zero, simulations are performed with PGopher software.[17] Since ground-state constants have not been reported for $HC_7D$ and $DC_7D$, the spectrum is analyzed starting from estimated values of $B_0''$ and $B_0'$, assuming that $B_e'/B_0'$ and $B_e''/B_0''$ ratios have similar values as for $HC_7H$ in Ref.[13] In addition, the value of the rotational groundstate constant of $HC_7D$, $B_e'' = 0.02706$ cm$^{-1}$ has been calculated at B3LYP/6-311++G$^{**}$ level using GAUSSIAN 03 software.[18] Guided by the simulated spectrum, in total 24 P-branch and 5 R-branch transitions are identified in the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ origin band of

**Table 1.** Derived constants for the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ electronic origin bands of $DC_7H$ and $DC_7D$, and a comparison with the isoelectronic species $HC_6N$, $DC_6N$ and $HC_7H$

| | $HC_7D$ | $DC_7D$ | $HC_7H$ | | $HC_6N$ | $DC_6N$ |
|---|---|---|---|---|---|---|
| $T_{00}{}^a$ | $19880.177(2)^b$ | $19943.184(5)^b$ | $19817.895(4)^c$ | $19817.892(2)^e$ | $21208.60(5)^f$ | $21282.10(5)^f$ |
| $B''_0$ | $0.027231(1)^b$ | $0.026216(2)^b$ | $0.028354(5)^c$ | $0.0283263(48)^e$ | $0.02806299(2)^d$ | $0.026982^f$ |
| $B'_0$ | $0.027133(1)^b$ | $0.026112(9)^b$ | $0.028221(4)^c$ | $0.0282298(46)^e$ | $0.02792(5)^f$ | $0.02682(5)^f$ |
| $D'' \times 10^8$ | $0.0343^d$ | $0.0343^d$ | $0.0343^d$ | $22.17(39)^e$ | $0.0343(17)^d$ | — |
| $D' \times 10^8$ | $0.0343^d$ | $0.0343^d$ | $0.0343^d$ | $28.12(36)^e$ | — | — |
| $B''_0/B'_0$ | 1.0036 | 1.0039 | 1.0011 | 1.0034 | 1.0051 | 1.006 |

All values are in $cm^{-1}$.

[a] The uncertainty in the band origin ($T_{00}$) represents the statistical error as obtained from the least-squares fit. The absolute laser frequency can be determined with a precision of $0.02\,cm^{-1}$.

[b] This work.

[c] Derived from a remeasured spectrum in this work.

[d] Ref.[19].

[e] Ref.[19]. Effective constants only.

[f] Ref.[20].

$HC_7D$. These transitions fully reproduce during independent scans. The unambiguous assignment of P($N$) lines for $N \leq 13$ in the best part of the spectrum, devoid of spectral lines pertaining to polluting species, warrants an accurate determination of the band origin for $HC_7D$.

The measured frequencies are used in the final least-squares fit to derive the value of molecular parameters of $HC_7D$. For this, the band origin ($T_{00}$) and rotational constants ($B''$ and $B'$) are fitted simultaneously. Inclusion of distortion constants, $D''$ and $D'$ (fixed to the values derived for $HC_6N$ in Ref.[19]) effectively improves the quality of the fit. The resulting parameters are listed in Table 1. Figure 2 shows the simulated stick diagram using these values. The simulation yields a rotational temperature of ~26 K for $HC_7D$ in the slit jet expansion. The resulting ground-state rotational constant, $B''_0 = 0.027231$ $cm^{-1}$, is close to the calculated value of $B''_e = 0.02706$ $cm^{-1}$. The origin band of the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ electronic transition of $HC_7D$ at 19880.18(2) $cm^{-1}$ is in agreement with the value reported in Ref.[12]

## *DC₇D*

The $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ origin band spectrum of $DC_7D$, recorded at a S/N of ~15, is shown in panel (a) of Fig. 3. As for $HC_7D$, the spectrum is blended by a number of overlapping narrow peaks that are reproduced for conditions of lower density and discharged current, not in favor of carbon chain formation, as shown in panel (b). The signal-to-noise ratio of the $DC_7D$ spectrum is less than found for $HC_7D$, but some individual transitions can be resolved and unambiguously resolved, in particular in the P-branch, therewith defining the position of the band origin. As stated before the effective spacing between strong transitions now amounts to about 4$B$. The rotational analysis of the data is carried out following a similar procedure as described for $HC_7D$. In total 14 P-branch transitions and 7 R-branch transitions have been assigned. The resulting parameters from a least-squares fit are listed in Table 1. The value for the ground state rotational constant derived for $DC_7D$, $B''_0 = 0.026216$ $cm^{-1}$, is close to the calculated value of $B''_e = 0.02605$ $cm^{-1}$. Figure 3 shows the simulated stick diagram of individual rotational transitions in P- and R-branch using the values listed in Table 1. Nuclear spin statistics are clearly involved now, making the transitions for even $N$ twice stronger than those for odd $N$ values. The band origin is found at 19,943.18(2) $cm^{-1}$, very close to the value reported in Ref.[12] From the observed spectrum we estimate a rotational temperature of about 30 K for $DC_7D$. The ratios of $B''_0/B'_0$ for $HC_7D$ and $DC_7D$ amount to 1.0036 and 1.0039, respectively, and indicate that the overall chain length slightly increases upon electronic excitation. These values are consistent with the ratio found for $HC_7H$ (1.0034), and are slightly smaller than that found for $DC_6N$ (1.0060) and $HC_6N$ (1.0051).[13,20]

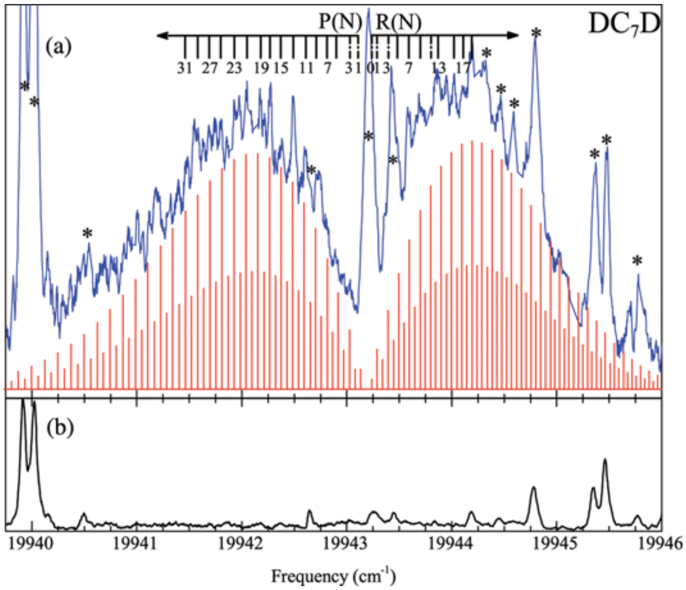

**Fig. 3.** (a) The observed rotationally resolved spectrum with simulated stick diagram of the $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ electronic transition of $DC_7D$. Peaks due to overlapping spectra originating from other species are marked by an asterisk and shown in panel (b) for expansion conditions not in favor of carbon chain formation.

In addition, the spectrum of $HC_7H$ is also remeasured with improved S/N level in the present work; the presently achieved S/N is ~35, while it was ~10 in the previous work.[13] With the remeasured spectrum, the molecular constants of $HC_7H$ have been improved and the results are summarized in Table 1.

### *Discussion*

Some weak additional features are observed in the experimental spectra of all the three species ($HC_7H$ [13], $HC_7D$ and $DC_7D$), particularly in the band origin regions where our spectra are not well resolved. This is likely a consequence of fine-structure effects, particularly prominent for transitions involving low rotational levels. For a $^3\Sigma$ electronic state, the spin-rotation constant, $\gamma$ is usually very small compared to $B$ and even for large $N$-values the resulting splitting of rotational levels will be difficult to resolve. The fine structure for the lowest $J$ values is significantly correlated with the value of $\Delta\lambda = \lambda' - \lambda''$. Therefore, the typical observation is an interfering intensity pattern due to overlap of lower $J$ rotational (small $N$) levels.

Another possible explanation of the complex spectral structures in the band origin regions is the likely spectral overlapping with other weak vibronic hot bands of the same species. A recent infrared study[21] on the polyacetylenes $HC_{2n}H$ in a similar plasma expansion has shown that, although a low rotational temperature can be achieved, the mode-dependent vibrational temperatures of $HC_4H$ and $HC_6H$ are found to be up to several hundred kelvin. However, without the knowledge of accurate ground-state spectroscopic parameters, the present experimental spectra do not allow to make a full analysis of these weak features. Future high-resolution infrared measurements on the $HC_7H$ ground state may improve the analysis of the present study.

In previous investigations indication was found for excited state lifetime broadening in $HC_7H$.[11,12] We have performed simulations for the presently obtained spectra of the deuterated species by convolving a Lorentzian width to the Gaussian width of $0.04\,\mathrm{cm}^{-1}$, the latter produced by the combined effects of laser line width and Doppler width. An optimum is found for a Lorentzian width of $0.02\,\mathrm{cm}^{-1}$, corresponding to an upper state lifetime of 0.3 ns. This lifetime, resulting from spectra of slightly higher quality, is somewhat larger than the indicative value of 0.1 ns reported by Ball et al.[12], but in view of the uncertainties associated with the overlapping structures still in reasonable agreement. It proves that nonradiative decay process occur for all three isotopologues.

## Conclusion

The present spectroscopic study on $HC_7D$ and $DC_7D$ radicals marks the limit of what can be achieved in terms of resolving rotational manifolds of chains of carbon-based hydrocarbons of increasing length under conditions of slit-jet discharge plasma expansions typically used in a number of laboratories to record optical absorption spectra of such species.[4,12,14,15] Where the rotational structure of $C_6H$ and $C_6D$ radicals could be fully resolved in a setup with a generic pulsed cavity ring-down experiment combined with a slit-jet discharge expansion[15], for the present chains with seven carbon atoms the rotational sequences become overlapped. In addition indication is found of broadening due to internal conversion of electronic excitation in $HC_7H$ and its deuterated analogs. The presently observed spectra display an improvement over to those of a previous investigation[12], just sufficient to extract values for the rotational constants of $HC_7D$ and $DC_7D$, providing insight in a change of chain length upon electronic excitation.

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