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Low temperature Raman spectra of cyanobutadiyne (HC_5N)

Michał Turowski[a,*], Claudine Crépin[b], Stéphane Douin[b], Marcin Gronowski[a], Isabelle Couturier-Tamburelli[c], Nathalie Piétri[c], Adam Wasiak[a,d], Robert Kołos[a,d]

[a] Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland
[b] Institut des Sciences Moléculaires d'Orsay, UMR 8214 CNRS, Université Paris-Sud, Bât. 210, 91405 Orsay, France
[c] Physique des Interactions Ioniques et Moléculaires, UMR 6633 CNRS, Université de Provence, Case 252, Centre de St. Jérôme, 13397 Marseille Cedex 20, France
[d] Cardinal S. Wyszyński University, Faculty of Mathematics and Natural Sciences, Wóycickiego 1/3, 01-938 Warsaw, Poland

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ABSTRACT

Low temperature Raman scattering spectra of cyanobutadiyne, either condensed from the vapour as a solid film, or isolated in a cryogenic argon matrix, have been measured – leading to the identification of all vibrational fundamentals, together with several overtones and combination modes. The analysis is based on previous experimental data, including the vibrationally resolved phosphorescence spectra, and on the comparison to available theoretical predictions.

1. Introduction

1-Cyano-1,3-butadiyne (hereafter referred to as cyanobutadiyne; other names: 2,4-pentadiynenitrile, cyanodiacetylene) has been detected in numerous extra-terrestrial environments, including the molecular clouds Sagittarius B2 [1] or TMC-1 [2], and circumstellar envelopes IRC+10°216 or CRL 618 [3,4]. It has also been found among the products of laboratory simulations of Titan's atmosphere [5,6]. Such long, rod-shaped molecules are also interesting from the purely spectroscopic point of view. Microwave rotational spectra of HC_5N (also in excited vibrational states) and high-resolution measurements of its ν_2 and ν_7 vibrational bands were reported [7–9]. Access to large quantities of the pure compound, and hence to its high quality UV, visible and IR spectra became possible with the discovery of an efficient synthetic route by Trollez and Guillemin [10]. Successively, the IR (in the 400–4000 cm^{-1} region [11]), mid-UV ($\tilde{A} - \tilde{X}$ and $\tilde{B} - \tilde{X}$ electronic systems [12]) and vacuum–UV ($\tilde{C} - \tilde{X}$ [13]) frequencies and absolute intensities of absorption bands were measured for gaseous samples. Independently, IR and UV absorption spectra have been reported for molecules isolated in rare gas matrices [12,14], and strong phosphorescence from the lowest triplet electronic state of HC_5N has been discovered in these cryogenic media [12].

Gas-phase measurements reported by Bénilan et al. [11] did not allow for the detection of far-IR bending modes ν_{10} and ν_{11}; the estimation of these frequencies proved nevertheless possible [12] via the analysis of electronic spectra. Theoretical calculations were carried out to predict the HC_5N geometry, rotational constants, harmonic and anharmonic vibrational frequencies, and IR intensities [9,15–18]. Gronowski and Kołos [19] published on the DFT estimations of Raman scattering activities. This work presents the complementary experimental information on vibrational modes of HC_5N, with the first measurement of its Raman spectrum. For reference, the displacement vectors for fundamental vibrations are presented in Fig. 1.

2. Experimental

Cyanobutadiyne was synthesized following the procedure reported by Trolez and Guillemin [10]. The typical HC_5N:Ar ratio in the gas mixture used for the cryogenic matrix deposition was 1:1000. HC_5N was evaporated to a gas manifold from a glass container maintained at −30 to −20 °C; argon (Multax 5.0 grade) was added up to a total pressure of 800–900 Torr. The mixture was then solidified onto a gold-plated copper substrate kept at about 7 K within a closed cycle two-stage helium refrigerator (Advanced Research Systems, DE-202SE). Alternatively, the mixture was

* Corresponding author. Tel.: +48 22 3433055; fax: +48 22 3433333.
E-mail addresses: mturowski@ichf.edu.pl, michal.turowski@op.pl (M. Turowski).

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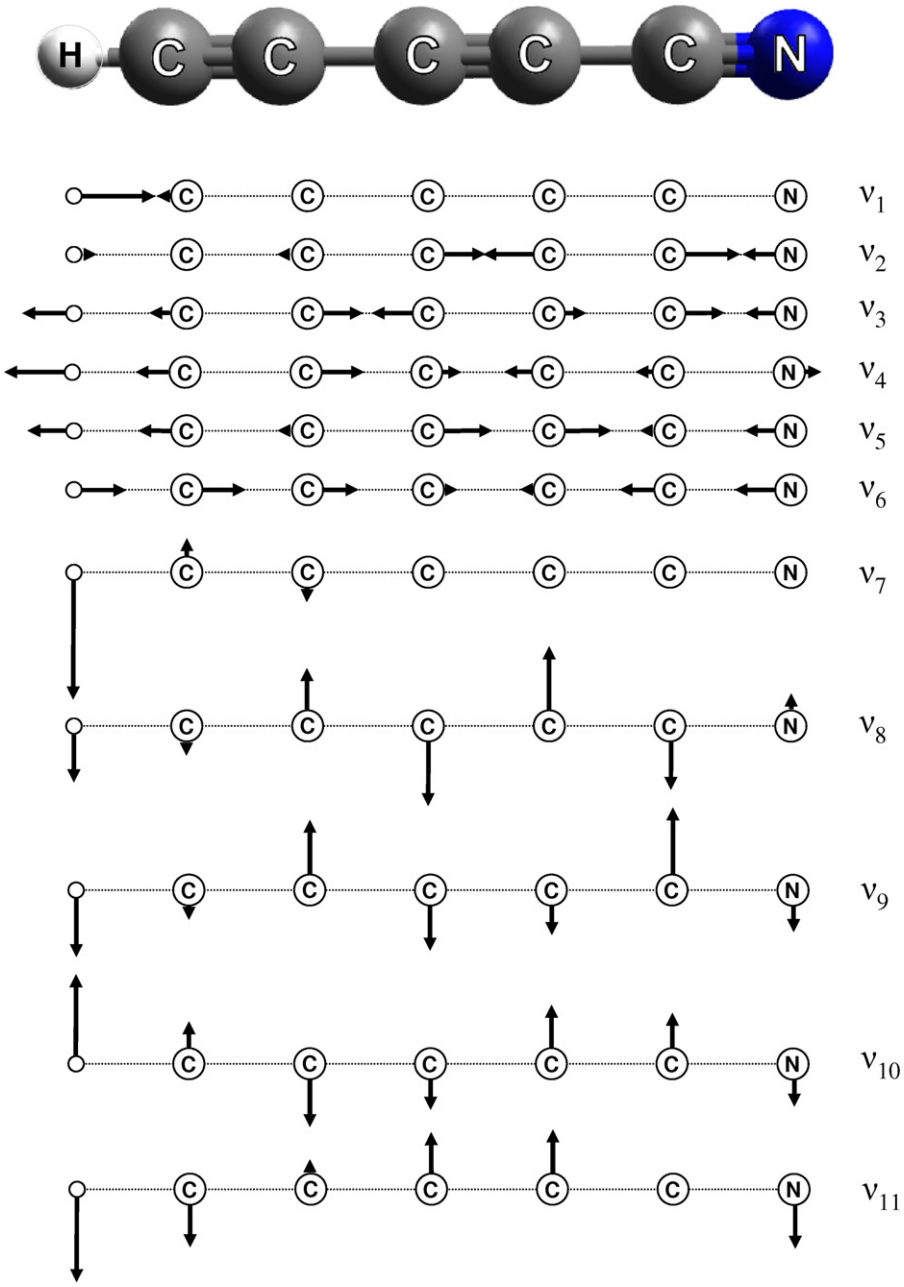

Fig. 1. Displacement vectors for fundamental vibrational modes of HC_5N in its ground electronic state, as predicted with the density functional theory (after Ref. [12]).

deposited onto a substrate held at ca. 60 K, which did not permit for the trapping of argon, and resulted in the formation of a pure solid HC_5N layer. The tip of the gas-delivering nozzle was located about 1.5 mm from the cold surface. The usual flow ratio was 0.01 mmol/min, the total amount of gas mixture entering the cryostat was about 0.3 mmol. Freezing gas formed a circular spot with a good visible transparency and variable thickness, the latter increasing (up to ca. 1 mm) towards the centre. Samples were analysed with a Renishaw *inVia* Raman microscope equipped with a 30 mm or 60 mm objective lens (Leica). A 1800 grooves/mm diffraction grating was usually employed, and wavenumber calibration accuracy was typically not worse than 1.5 cm^{-1}. A laser-illuminated part of the sample, the source of scattered light, had the diameter of ca. 20 μm. The best quality of spectra (and the resolution of about 5 cm^{-1}) was obtained with a helium-neon laser (632.8 nm; Renishaw W633). This light source has been used for the excitation throughout the entire Raman spectrum, with the exception of C—H stretching region around 3300 cm^{-1}, where a 514 nm Ar ion laser line (Modu-Laser, *Stellar-REN*) offered a better signal-to-noise ratio (with a resolution of about 6 cm^{-1}). Spectral features not due to Raman scattering were identified as such by their variable shift from the excitation wavenumber, dependent on the choice of the laser and/or on the monochromator setting.

3. Results and discussion

Various HC_5N/Ar ratios could be obtained for the solidified sample in our matrix-isolation studies, depending on the temperature of the substrate plate and on the rate of the gaseous mixture deposition. This allowed for the measurements of either separated or