On the role of molecular clustering on infrared absorption line shapes of acetylene in a supersonic expansion

K. Didriche, C. Lauzin, P. Macko 1, W.J. Lafferty 2, R.J. Saykally 3, M. Herman *

Laboratoire de Chimie Quantique et Photophysique, CP160/09, Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Avenue Roosevelt, 50, B-1050 Brussels, Belgium

1. Introduction

We have recorded the $v_1 + v_2$, 2CH-stretch band of jet cooled acetylene around 1.5 μm, using ultrahigh sensitivity CW-cavity ring down spectroscopy (CW-CRDS). We observed unusual line profiles, all very broad and some further demonstrating a central dip when recorded in a free expansion produced from a circular nozzle. Similar observations were already reported in the literature for other species (see e.g. [1–5]). The broadening was attributed to the combination of the cone angle in the expansion, inducing a specific Doppler shift, and of the molecular density, contributing a specific weight to the absorption intensity. This effect was quantified in [5]. The central dip was tentatively assigned to the presence of the molecular clusters in the central, denser part of the jet, in [2,4], thus removing absorption intensity from the monomer line at zero Doppler shift. We further investigate these phenomena in this study, for the first time with acetylene.

2. Experimental set-up

The CW-CRDS facility available within the FANTASIO experimental set-up, for ‘Fourier trAnSform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansion’, was used in this work. All details concerning FANTASIO are provided in [6]. We only recall here that the continuous supersonic expansion, which is perpendicular to the CW-CRDS probe beam, is produced using a turbo pump (Leybold MAG W3200 CT). Circular or slit nozzles were used, respectively made of stainless steal and brass. The CRDS laser beam was set 1 mm below the nozzle. Whenever relevant, dry N2 was gently flowing in tubes fixed to the CRDS mirrors and ending at the expansion cone to prevent absorption from residual, warm acetylene. Various injection conditions of acetylene, pure or seeded into Ar or into He, were used, representing a compromise between optimal signal to noise ratio and adequate spectral comparison criteria.

CRDS absorption coefficients are determined directly from the data, as explained in [6]. The diode laser contribution to the line-width in these experiments is estimated to be smaller than 1 MHz and is therefore neglected.

3. Acetylene line shapes

The anomalous line shapes are exemplified in Fig. 1, which presents $R(J)$ lines in $v_1 + v_2$, recorded in an acetylene/Ar expansion produced from a circular nozzle. They show a constant, broad width of the order of 450 MHz (FWHM) and a central dip with $J$-dependent depth. These four lines will be used in the procedure hereafter. They are actually from $^{12}\text{C}^{13}\text{CH}_2$, observed in natural abundance (2%), thanks to the instrumental sensitivity. These are preferred to those from $^{12}\text{C}^{12}\text{CH}_2$, because they are weaker and thus more likely to be free from saturation effects. Only nuclear spin effects would differ, but this was not observed.

One can calculate the angular distribution of the species in the flow, from the simple and fully empirical model of Ashkenas and Sherman [7]

$$\frac{\rho(y,x)}{\rho(0,x)} = \cos^2 \theta \cos^2 \left( \frac{\pi \theta}{2 \phi} \right)$$

(1)

with $\theta$, the angle with respect to the X central axis in the conical expansion, and $\rho(y,x)/\rho(0,x)$, the molecular density at a distance
The optimal agreement was found for the symmetric, outer concentration of acetylene, which was imposed in the final stage of the procedure. It first confirms the known Doppler analysis of line profiles in expansions from circular nozzles, subsequently assuring the role of clustering processes, occurring in the central part of the expansion, on monomer line profiles. This role, which was only suggested in the previous literature, is now partly quantified. The difference between line intensities simulated without and with clustering was calculated. It appears to be regularly decreasing between 64% and 39% from \( R(0) \) to \( R(3) \). It thus appears that increasing rotational angular momentum hinders the clustering process. A complementary effect is apparent from Fig. 2, which presents a Boltzmann plot accounting for the relative evolution of the amplitude of the central Gaussian contribution to the reconstructed line profile. The plot indeed converges towards a rotational temperature slightly but significantly warmer than that controlling the evolution of the outer Gaussian contributions to the observed line shapes. As previously mentioned, the latter was set to 6 K. The rotational temperature increase, thus estimated to some 5 K, must be induced by heat release during the clustering process.

The reconstructed line profiles and the sets of Gaussian contributions are also detailed in Fig. 1. Although not demonstrated in Fig. 1 for clarity, the triple contribution also allows the expected unperturbed line profile to be matched. It is simply required to increase the amplitude of the central Gaussian contribution, not modifying its width, nor changing the outer contributions.

### 4. Discussion

The agreement between observed and simulated line profiles in Fig. 1 is very reasonable, despite the various assumptions in the procedure. It first confirms the known Doppler analysis of line profiles in expansions from circular nozzles, subsequently assessing the role of clustering processes, occurring in the central part of the expansion, on monomer line profiles. This role, which was only suggested in the previous literature, is now partly quantified. The difference between line intensities simulated without and with clustering was calculated. It appears to be regularly decreasing between 64% and 39% from \( R(0) \) to \( R(3) \). It thus appears that increasing rotational angular momentum hinders the clustering process. A complementary effect is apparent from Fig. 2, which presents a Boltzmann plot accounting for the relative evolution of the amplitude of the central Gaussian contribution to the reconstructed line profile. The plot indeed converges towards a rotational temperature slightly but significantly warmer than that controlling the evolution of the outer Gaussian contributions to the observed line shapes. As previously mentioned, the latter was set to 6 K. The rotational temperature increase, thus estimated to some 5 K, must be induced by heat release during the clustering process.

We have previously reported on the observation of acetylene-Ar complexes using FANTASIO under very similar experimental conditions, with 9 K rotational temperature [8]. Fig. 3 compares...
lines from Acetylene–Ar recorded in the same 1.5 μm spectral range using CW-CRDS using either slit or circular nozzles. The Doppler doubling of the lines in the latter case demonstrates that the complex is formed at the edge of the conical expansion. Transforming the Doppler shift once more into angular dependence leads to 45°. This angle is thus larger than for the outer acetylene contributions in Fig. 1 (32°). Acetylene–Ar therefore cannot be responsible for the removal of acetylene monomers at the expansion centre. The formation of acetylene–Ar complexes could nevertheless lead to heat acetylene monomers in the outer part of the expansion. This effect must, however, be very limited given the weak dissociation energy of the complex. It is, in any case, already included in the 6 K rotational temperature associated to this portion of the expansion.

The role of acetylene multimers in the central dip is demonstrated in Fig. 4, which presents the weaker and non-saturated $R(0)$ line in $v_1 + v_3$ band of jet-cooled $^{12}$C$^{13}$CH$_2$. The observed central dip can here only be attributed to the presence of acetylene multimers. We checked the validity of the procedure demonstrated in Fig. 1 on the data of Fig. 4. It indeed produces about identical results, including the angular distribution of the three contributing Gaussian shapes. As additional evidence for the presence of acetylene aggregates, besides a previous literature report [9], we directly observed several unresolved absorption features, identical in acetylene–Ar and acetylene–He circular nozzle expansions, using CW-CRDS. They can only be attributed to acetylene aggregates. These spectral features could actually only be resolved using CW-CRDS in a slit nozzle jet. The resulting structure is shown in Fig. 5 for one of the bands attributed to acetylene multimers, observed around 6542 cm$^{-1}$. Strong spectral congestion and weak line intensities are observed, explaining why the structure cannot be resolved under circular nozzle conditions.

We tentatively assigned the absorption feature in Fig. 5 to the $K_a = 2–3$ sub-band of the acetylene dimer, by comparison with the simulation performed using ground state constants from the literature [10], also presented in Fig. 5. There are two of the 18 bands attributed to the $v_1 + v_3$ band of jet-cooled $^{12}$C$^{13}$CH$_2$. Strong spectral congestion and weak line intensities are observed, explaining why the structure cannot be resolved under circular nozzle conditions.

The role of acetylene multimers in the central dip is demonstrated in Fig. 4, which presents the weaker and non-saturated $R(0)$ line in $v_1 + v_3$ band of jet-cooled $^{12}$C$^{13}$CH$_2$, recorded in an expansion of pure acetylene from a slit nozzle (20 × 0.3 mm), $p_0 = 859.93$ hPa, $p_1 = 3.3$ Pa; acetylene/Ar flow = 40/1810 sccm.
these sub-bands presumably due to tunnelling effects. Since various sizes of aggregates can be expected to be formed in the expansion, one cannot attempt relating the energy release previously mentioned to a specific step in the acetylene nucleation process.

In conclusion, we have investigated an expansion of acetylene and Argon from a circular nozzle using CW-CRDS in the 1.5 μm spectral range. It is now clearly demonstrated that the aggregates produced in the expansion are responsible for central dips observed in the monomer absorption lines. Only acetylene aggregates are to be accounted for in this process since acetylene–Ar complexes appear to be formed at the edge of the conical expansion. It can even be tentatively suggested that the acetylene aggregates are localised within a cone around the central expansion with 16° (HWHM) aperture, leading to some 5 K rotational temperature heating.

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