$^{12}C_2H_2$−Ar van der Waals complex

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New theoretical and experimental results on the acetylene−Ar van der Waals complex are presented and the literature is reviewed. New ab initio calculations at the MP2 level were performed using large basis sets with diffuse functions and taking into account the basis set superposition error. It was found that the structure of acetylene is not significantly altered by the complexation and that its vibrational frequencies are only slightly lowered. Finally, it was observed that the calculated properties of the complex (structure, vibrational spectrum, bond dissociation energy) are not sensitive to the structure imposed on acetylene. Experimentally, acetylene−Ar was produced in a supersonic expansion under experimental conditions corresponding to 9 K rotational temperature. Thanks to the performances of CW-CRDS detection, the $K_a = 0 \leftarrow 1$, $1 \leftarrow 0$, and $2 \leftarrow 1$ sub-bands of the $\nu_1 + \nu_3$ band could be recorded and resolved and most of their lines assigned. Upper-state rotational constants were fitted, however not including the upper $K_a = 2$ state, which shows K-doubling the opposite of the expected. The Lorentzian width of most line profiles sets the mean lifetime to some 7.5 ns. Local perturbations affecting line positions and/or line widths are demonstrated. Additional series of lines tentatively attributed to acetylene−Ar are discussed.

1. Introduction

The acetylene−Ar complex presents a so-called pathologically flat potential,[1] making ab initio calculations very challenging. The intermolecular potential energy surface (IPES) was first investigated by Kisiel[2] and by Le Sueur et al.,[3] in 1991, from a distributed multipolar analysis. The IPES was empirically determined by Thornley and Hutson, in 1992, from the existing spectroscopic data.[4] Next year, associated to their experimental investigation, Bemish et al. (1993) calculated a semiempirical IPES by combining experimental data and self-consistent field ab initio calculations.[5] Yang and Watts in 1994 improved this potential with the help of scattering data.[6] In the same year, Bone calculated an ab initio IPES at the second-order Møller−Plesset perturbation theory (MP2).[1] He found four stationary points on the surface. Tao et al. in 1995 proposed an improved potential calculated at the MP4 level of theory with a rather large basis set (triple-ζ) containing bond functions.[7] They determined rovibrational spectroscopic constants using the collocation method. Yang et al. in 1996 calculated a better potential with the coupled cluster method with single and double excitations augmented by a perturbational estimate of the effects of connected triple excitations (CCSD(T)).[8] They used the Dunning's aug-cc-pVTZ basis set[9,10] and midbond functions. Hasse et al. in 1996 recalculated the IPES using the supermolecular Møller−Plesset perturbation theory and the CCSD(T) method with the aug-cc-pVTZ basis set and midbond functions.[11] More recently (2005), the IPES was improved by Munteanu and Fernandez at the CCSD(T) level using the larger aug-cc-pVQZ basis set extended with midbond functions.[12] Finally, Cappelletti et al. proposed a semiemprical IPES using new scattering data and pressure broadening coefficients.[13,14]

The acetylene−Ar van der Waals molecular complex was spectroscopically investigated in various spectral regions. In the microwave range, after initial studies by DeLeon and Muenter in 1980[15] and by Endo and co-workers,[16] Liu and Jäger reported precise rotational constants from pure rotation spectra in various isotopologues in 2001.[17]

In the infrared range, the fundamental cis-bending acetylenic excitation was investigated by Ohshima and co-workers in a series of papers starting in 1988.[16,18−20] The fundamental antisymmetric CH excitation was studied by Muenter, Howard, and their co-workers in 1992, using diode lasers and multipass optics[21] and, in 1993, by Miller and co-workers using diode lasers now with optothermal detection.[5] The latter authors investigated, among several other issues, the role of anharmonic resonances in the parent species in promoting vibrational predissociation.[22] All of these investigations confirmed the extremely floppy character of the complex.

The experimental structure, thus characterizing the molecule above the very shallow minimum appears to be strictly T-shaped. This is supported by the 1:3 intensity alternation typical of the ethyne or acetylene subunit in the spectra, indeed implying a symmetric (C_{2v}) structure with identical hydrogen atoms. It is further supported by the selection rules behind the observed transitions reported in the literature, involving electric dipole moments parallel or perpendicular to the acetylene subunit only.

Despite the very floppy character of the complex, thus confirmed by the various experimental and theoretical results, the experimental literature indicates that acetylene−Ar is stable enough to be observed in the overtone range, that is around 1.5 μm.[23,24] The 2CH acetylenic overtone excitation, around 1.5 μm, was indeed reported in 1996 by Orr and collaborators.[23] The information published at the time was however limited to band

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shapes showing the *K*-structure of the overtone transition. We recently further reported on new, preliminary results concerning the observation of the $^{12}C_2H_2$−Ar complex in this 1.5 μm overtone region, at high spectral resolution, using CW-cavity ring down spectroscopy (CW-CRDS).[24]

To complete this literature survey, one should also mention several reports on Ar-induced collision effects on vibrationally excited acetylene (e.g., refs 6, 14, 25−29).

Acetylene−Ar is thus a very interesting system, which is further investigated in the present contribution, theoretically and experimentally. In section 2, specific problems around the equilibrium structure and fundamental vibrations issues are addressed, from new ab initio calculations. The remainder of the article, of experimental nature, focuses on the overtone range. In section 3, the experimental setup is detailed. The spectral analysis is presented and discussed in sections 4 and 5, respectively. A general conclusion appears in section 6.

2. Ab Initio Computations

As mentioned above, Munteanu and Fernandez[12] determined an accurate IPES. However, they assumed that the structure of the acetylene subunit remained unchanged upon complexation. Furthermore, they adopted a (r_0) structure significantly different from the equilibrium structure of the monomer, which is r_e(CC) = 1.2029 Å and r_e(CH) = 1.0618 Å.[30] Although the first assumption is likely to be reasonable for a weak complex as acetylene−Ar, it is not obvious that the computed properties of the complex will not be affected by the initially selected structure. For this reason, we optimized by means of second-order Møller−Plesset perturbation theory (MP2)[31] the structure of the complex without any constraint, and we compared it to that of the monomer calculated at the same level of theory. The Dunning's correlation consistent polarized and augmented basis sets (aug-cc-pVXZ, with X = T and Q, hereafter denoted as AVXZ) were used[9,10] for describing the acetylene moeity, and the improved version of the Dunning's basis sets with extra tight *d* polarization functions, AV(X+d)Z, with X = T and Q[32] for argon. The BSSE was taken into account in all calculations by the counterpoise (CP) correction.[33] Calculations were performed with *Gaussian 03*[34] and *MOLPRO* suites of programs[35−37] running on the HP-XC 4000 cluster of the ULB/VUB computing center.

It was indeed confirmed for X = T and Q that the geometry of the acetylene subunit in the complex is very close (within 2.10^{-4} Å) to that of the isolated monomer at the same level of theory. Furthermore, we found that the binding energy and the complex geometry were practically unchanged when imposing the r_0 structure instead of the equilibrium structure.

The MP2/AV(Q + d)Z surface has been calculated. The skew T-shaped equilibrium structure of the C_2H_2−Ar complex is confirmed with, at the present level of calculation, the two minima corresponding to geometries of **R** = 3.9 Å and θ = 64 and 116° and to an energy of −145.75 cm^{-1}, thus close to the optimal values of Munteanu and Fernandez[12] (**R** = 3.99 Å, θ = 60.6 and 119.4°, and minimum of energy at −122.17 cm^{-1}). The topology of this double minima surface is illustrated in Figure 1, where the interaction energy is plotted against **R** and θ, the two geometrical parameters defining the position of the argon atom with respect to the acetylene subunit (inset of the Figure). The barrier at θ = 90° is calculated to be 6 cm^{-1}, again close to the one obtained by Munteanu and Fernandez (8.33 cm^{-1}).[12]

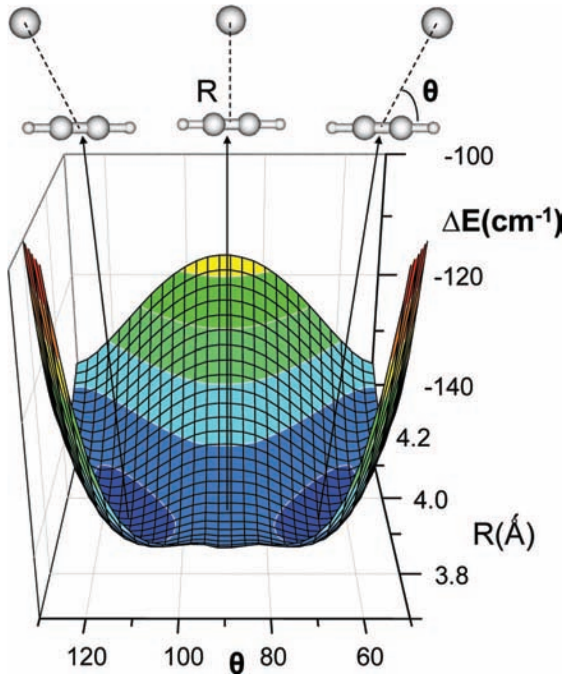

Figure 1. Plot of the interaction energy as a function of θ and **R** for acetylene−Ar, at the MP2/AV(Q + d)Z level of calculation for a fixed linear HCCH moiety.

TABLE 1: Harmonic Frequencies and Fundamental Band Intensities of the Skew T-Shaped Structure of the Acetylene−Ar Complex from Ab Initio Calculations; the Corresponding Values for the Monomer Are Listed in Parentheses

	harmonic frequencies (cm^{-1})			intensities (mol km^{-1})[b]
ref[a]	L	L	B	L
method	MP2	MP2	MP2	MP2
basis set	AV(T + d)Z	AV(Q + d)Z	TZ	AV(Q + d)Z
ω_1	3533.2	3530.0	3519	0.03
	(3533.6)	(3530.3)		(0.0)
ω_2	1967.1	1974.1	1976	0.01
	(1967.9)	(1974.15)		(0.0)
ω_3	3431.3	3442.5	3432	93.0
	(3431.6)	(3442.6)		(95.5)
ω_4'	599.9	612.1	472.5	84.4
	(601.4)	(612.6)		(89.0)
ω_4''	600.5	612.6	477	96.5
	(601.4)	(613.6)		(89.0)
ω_5'	753.6	750.0	713	0.08
	(753.9)	(750.3)		(0.01)
ω_5''	753.7	750.1	713	0.01
	(753.9)	(750.3)		(0.01)

[a] L: Lauzin et al., this work; B: Bone, ref 1. [b] Fundamental bands' infrared intensities calculated within the double harmonic approximation.

We also calculated the vibrational spectrum for the equilibrium structure at the harmonic level using the MP2/AV(X + d)Z method (with X = T and Q). The results are summarized in Table 1. It can be checked that the difference between the two basis sets is only a few wave numbers, the largest difference being 12 cm^{-1}. For completeness, one should mention the experimental values of the bands reported in the literature: ν_5" = 730.6582 cm^{-1}, ν_5' = 730.7961 cm^{-1} [20]; ν_3 = 3294.471 cm^{-1}, $\nu_2 + \nu_4 + \nu_5$ = 3281.537 cm^{-1} [21] and, from the present results (section 4), $\nu_1 + \nu_3$ = 6555.4692 cm^{-1}.

The low-frequency vibrations are unfortunately not considered in these calculations because they correspond to large amplitude motions that cannot be described correctly by the procedure

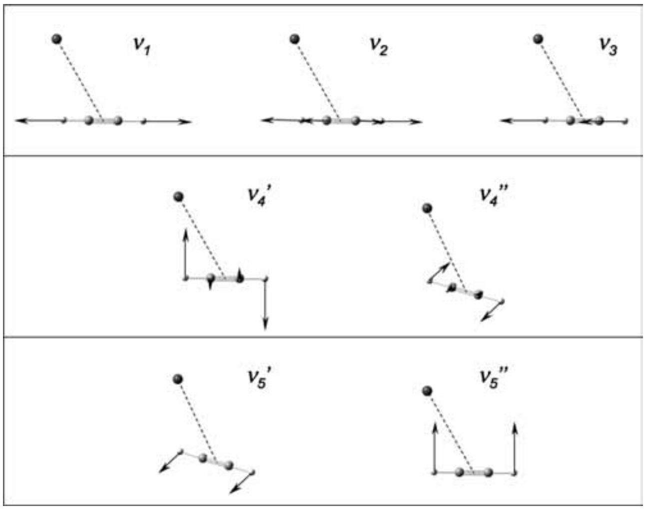

Figure 2. Normal modes of the acetylene−Ar complex calculated at the AV(Q + d)Z/MP2 level of approximation (Table 1 for the corresponding harmonic frequencies). Atomic displacements are scaled by a factor of 2 for all modes. Only modes of the parent acetylene species are represented.

implemented either in *Gaussian 03*[34] or *MOLPRO*, which assumes that the amplitude of the vibrations is small. Experimentally, the value $\nu_{\mathrm{bend}} = 6.222$ cm^{-1} was reported from the experimental observation of a combination band in the 3.3 μm range, by Miller and co-workers, leading to[5] and later supported by theoretical results.[7] It confirms the estimation (8.9 cm^{-1}) by Ohshima et al.[19] from the analysis of the experimental centrifugal distortion constants. The latter authors also estimated $\nu_{\mathrm{stretch}} =$ 36.6 cm^{-1}, using the same method.

The calculated modes are displayed in Figure 2. These are harmonic modes characterizing the equilibrium structure. As the top of the barrier to internal rotation is only 6 cm^{-1} above the potential minimum, the ground vibrational level is above it, and therefore the molecule is T-shaped in the ground state, as reported from the experiments. The nuclear movements are however not significantly affected by this change. Actually, they all are almost identical to those of the acetylene subunit represented in refs 38 and 39. The difference between the corresponding harmonic frequencies of the complex and of the acetylene monomer is extremely small, as also shown in Table 1. We also attempted to calculate the energy of the $\nu_1 + \nu_3$ vibrational state, which is concerned with the experimental observations described in the next sections. The calculated value is lower than the experimental one by 0.77 cm^{-1} at the AV(Q + d)Z level and 0.39 cm^{-1} at the AV(T + d)Z level, assuming that the anharmonicity remains constant upon complexation. These variations are however barely significant within the present approximations.

The intensities of the fundamental bands in the complex calculated in the doubly harmonic approximation are also given in Table 1. They are quite close to those of the acetylene monomer.

3. Experimental Details

A new setup developed in Brussels, named FANTASIO, for "Fourier trANsform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn",[40] was used to perform a preliminary investigation of acetylene−Ar in the overtone range.[24] This was actually the first time a weakly bound complex was experimentally investigated in our group, beyond N_2O_3[41] and N_2O_4.[42] We have since improved the spectral coverage and the signal-to-noise ratio, varied the injection conditions in the supersonic expansion, and reconsidered the calibration and line measurement procedures, altogether allowing a significant number of new spectral features to be observed, measured, and investigated.

It is worth reminding that the FANTASIO setup includes a main vacuum chamber in which the continuous supersonic expansion is produced thanks to a turbo pump (Leybold MAG W3200 CT, Teflon coated), backed by a dry pump group (Alcatel ADS 860 HII). A slit nozzle (∼10 mm × 0.5 mm) was used, made of brass. The reservoir (p_0) and residual (p_∞) pressures were measured using MKS Baratron gauges (1000 and 1 Torr full scale, respectively). The p_0/p_∞ pressure ratios were varied between 20 000 and 35 000. Acetylene (from Air Liquide with 99.6% stated purity) seeded into Ar was used. Optimal S/N was typically observed for acetylene/rare gas proportions of 1:100. The studied and carrier gas flow were measured using MKS and Brooks flowmeters (10 000 and 30 000 sccm full scale, respectively). A single spectrum was selected for all figures in the experimental section, with the following experimental conditions: $p_0 = 860$ hPa, $p_\infty = 3.3$ Pa; acetylene/Ar flows = 1%.

We shall here report on results recorded using only one of the probe techniques available within FANTASIO, that is CW cavity ring down spectroscopy (CW-CRDS). These experiments were performed using a diode laser emitting in the 1.5 μm range (DFB, ILX lightwave, 1 MHz line width). It was temperature tuned in the 6544.8 to 6579.3 cm^{-1} spectral range. In the setup, the diode beam is sent through an optical isolator (Thorlabs 4015 5AFC-APC) and then split to enter both a homemade Fabry-Pérot etalon providing an FSR of about 955 MHz (1%) and an acousto-optical modulator (AOM) from AA Opto-Electronic (MGAS 80-A1) (99%). A series of two lenses ($f_1 =$ 30 mm, $f_2 = 50$ mm) and two flat mirrors is used to inject the order 1 output from the AOM into the TEM$_{00}$ mode of a linear ring-down cavity mounted around the expansion. This optical cavity is made of two concave mirrors (radius = 1000 mm, reflectivity = 99.988%), separated by about 540 mm. The output coupler is fixed on a piezo system driven at some 500 Hz (Piezomechanik HPST 1000/15−8/5). The light exiting the cavity is focused through a lens ($f = 20$ mm) on a InGaAs photodiode (type PT511, 300 μm, TO-4G flat window). The signal from the photodiode is converted by a trans-impedance amplifier (OPA627). Cavity mode matching, achieved at twice the selected frequency, triggers the measurement procedure. Typically, some 100 ring-downs per spectral point are fitted and their mean ring-down time (τ) is recorded. The absorption coefficient α is directly calculated using:[43]

$$\alpha = \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)\frac{L}{cl} \qquad (1)$$

in which τ_0 is the ring-down time in an empty cavity (i.e., without absorber), L and l are respectively the lengths of the cavity and the absorption path in the medium, and c is the speed of light. The typical ring-down time is about 15 μs, corresponding to some 8333 passes, that is ∼80 m effective absorption path length in the jet-cooled molecules when using the 1 cm slit nozzle.

The experimental conditions were tuned to optimize the acetylene−Ar signals. The vertical distance separating the nozzle exit from the multiprobe plane, which can be varied between approximately 0 and 35 mm by stretching the bellow supporting the nozzle, was set as close as possible to the slit, that is about 2 mm below it. One should also mention that the linearization

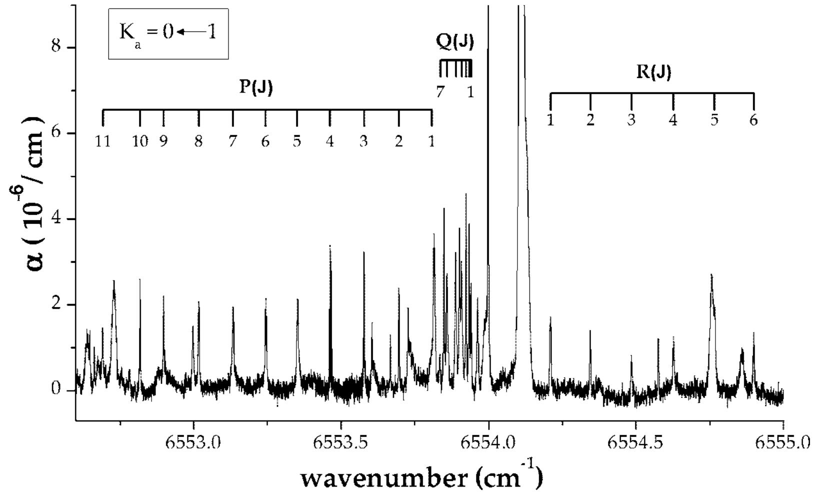

Figure 3. Overview of the $K_a = 0 \leftarrow 1$ sub-band in the 2CH band of the $^{12}C_2H_2$–Ar van der Waals complex recorded using CW-CRDS.

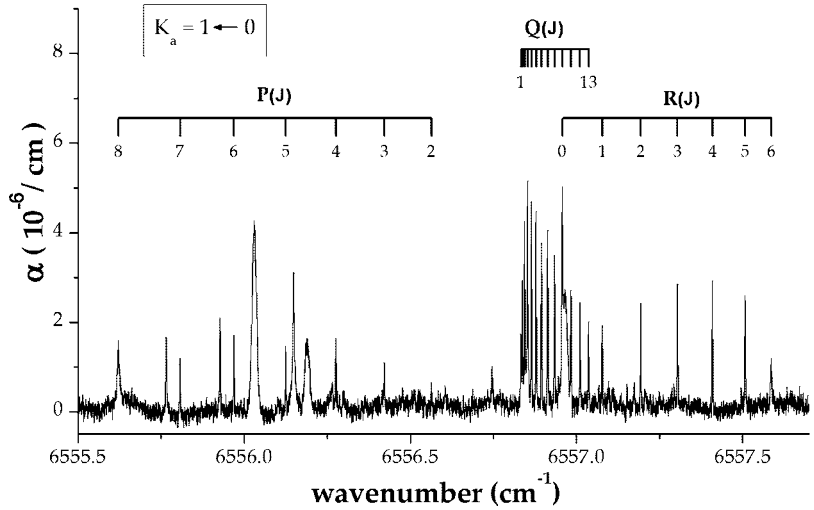

Figure 4. Overview of the $K_a = 1 \leftarrow 0$ sub-band in the 2CH band of the $^{12}C_2H_2$–Ar van der Waals complex recorded using CW-CRDS.

of the frequency scale of spectra has been done against the interference fringes of the Fabry-Pérot etalon built within FANTASIO. Then the spectra have been absolutely calibrated using acetylene monomer lines as references, from ref 44. The measurement precision and accuracy was improved compared to our previous report.[24] They are estimated to 5×10^{-4} and 10^{-3} cm^{-1}, respectively. A Voigt function has been fitted to match the line profiles. The resulting Lorentzian contribution to the line broadening is discussed in section 5.

Various series of lines were identified on the spectra according to their intensity behavior relative to the experimental conditions. As it turns out, different molecular carriers are involved, including acetylene multimers. We only considered here those lines that could be unambiguously attributed to acetylene–Ar. The additional species, as well as the acetylene–Ar jet dynamics are discussed in another paper.[45]

4. Spectral Analysis

The observed band corresponds to $\nu_1 + \nu_3$ as defined in Figure 2, that is to a 2CH excitation. The main spectral pattern could be readily identified using the results from the lower resolution spectrum in,[23] in terms of the $K_a = 0 \leftarrow 1$, $1 \leftarrow 0$, and $2 \leftarrow 1$ sub-bands. The main *a* axis of this T-shaped near prolate top lies in the acetylene–Ar plane, going through Ar and perpendicularly to the HCCH linear geometry (Figure 1). The acetylenic 2CH excitation band is of *b* type, thus with ΔK_a and ΔK_c odd, and $\Delta J = 0, \pm 1$. Nuclear spin statistics (3:1) favors odd versus even K_a values in the ground vibrational state. The spectral pattern in the 1.5 μm range presently studied is actually strikingly similar to the one in the 3 μm range reported in the literature,[5,21] but for the presence of only one main band of the parent species in the present region, $\nu_1 + \nu_3$ $^{12}C_2H_2$, compared to two equally strong bands in the lower energy range, ν_3 and $\nu_2 + \nu_4 + \nu_5$.[46]

Portions of the overtone spectrum presently recorded are displayed in Figures 3, 4, and 5. The analysis of the $K_a = 0 \leftarrow 1$ and $1 \leftarrow 0$ sub-bands was completed compared to our previous report,[24] whereas the analysis of the $K_a = 2 \leftarrow 1$ sub-band is reported here for the first time. A detailed comparison between the spectra recorded using various experimental conditions showed that some unassigned lines that were initially associated to acetylene–Ar are likely to belong to other species formed in the expansion. Some of these extra lines are identified in Figure 5.

The lines were assigned within each sub-band using ground-state combination differences calculated from the literature rotational constants.[17] Whereas the $K_a = 0 \leftarrow 1$ and $1 \leftarrow 0$ sub-bands could be simultaneously fitted in ref 24 using a conventional Watsonian in I^r representation with S-reduction,[47] a fit considering simultaneously all three sub-bands could not

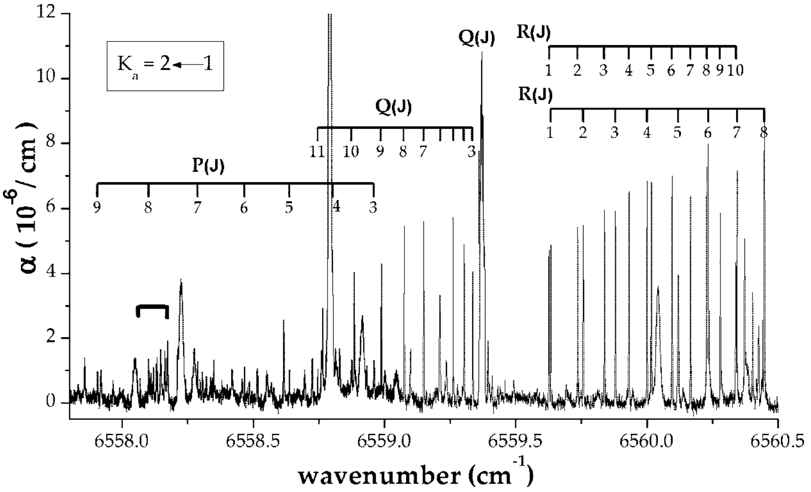

Figure 5. Overview of the $K_a = 2 \leftarrow 1$ sub-band in the 2CH band of the $^{12}C_2H_2$−Ar van der Waals complex recorded using CW-CRDS. A series of lines attributed to acetylene−Ar but unassigned is highlighted.

TABLE 2: Rovibrational Constants (in cm^{-1}) of the 2CH Vibrational Band of the $^{12}C_2H_2$−Ar van der Waals Complex Determined by Fitting Lines in the $K_a = 0 \leftarrow 1$ and $1 \leftarrow 0$ Sub-Bands of the 2CH Vibrational Band, Identified in Table 4

	lower state[a]	upper state
A	1.5861	1.4258 (25)
B × 10^2	6.9214	6.854 (94)
C × 10^2	6.1943	6.0635 (79)
$\mathbf{D_J}$ × 10^7	9.9	14.4 (42)
$\mathbf{D_{JK}}$ × 10^4	7.073	−2.56 (76)
$\mathbf{H_J}$ × 10^{11}	−7.0	−7.0[b]
$\mathbf{H_{JK}}$ × 10^7	−8.4	−8.4[b]
$\mathbf{d_1}$ × 10^7	−2.7	−2.7[b]
$\mathbf{h_1}$ × 10^{10}	5.0	5.0[b]
	$\tilde{\nu}_0 = 6555.4692$ (18), $\sigma = 4.9 \times 10^{-3}$	

[a] Constrained from Liu and Jäger, ref 17. [b] Constrained to lower state values.

TABLE 3: Energies (in cm^{-1}) of the Observed Upper Levels J, $K_a = 2$, K_c, in the 2CH Vibrational State of the $^{12}C_2H_2$−Ar van der Waals Complex

J	Ka	Kc	$\tilde{\nu}$
2	2	0	6561.281
2	2	1	6561.281
3	2	1	6561.656
3	2	2	6561.657
4	2	2	6562.157
4	2	3	6562.158
5	2	3	6562.782
5	2	4	6562.784
6	2	4	6563.529
6	2	5	6563.536
7	2	5	6564.398
7	2	6	6564.410
8	2	6	6565.387
8	2	7	6565.412
9	2	7	6566.495
9	2	8	6566.538
10	2	8	6567.712
10	2	9	6567.783
11	2	9	6569.045
11	2	10	6569.167

reproduce the line wavenumbers within the measurement precision. For reasons discussed in the next section, we decided to simultaneously fit the $K_a = 0 \leftarrow 1$ and $1 \leftarrow 0$ sub-bands, only, as in ref 24. The distortion constants that appeared to be determined with a precision better than their value were kept in the final procedure. The constants are listed in Table 2. The list of assigned lines, including those unfitted reaching $K'_a = 2$, can be obtained from the authors.

5. Discussion on the Experimental Results

As mentioned in the previous section, sub-bands with upper values of $K_a = 0$ and 1 present a structure typical of an asymmetric top, as in the lower energy ranges.[5,17,20,21] It turns out that K-splitting in the upper $K_a = 2$ substate is opposite to the one predicted for an asymmetric prolate top, explaining why the related lines could not be fitted simultaneously with the other sub-bands. The related upper state energies are listed in Table 3. Whenever the same level is observed in two different transitions, the mean value is selected. A similar behavior was already reported for other vibrational states of acetylene−Ar, initially by Hu et al.[21] and explained in terms of the floppy character of this complex in ref 4. The limitations of the rotational Hamiltonian used are confirmed by the anomalous values/signs of the distortion constants. This modeling problem also prevents the values of the resulting principal rotational constants to be compared for the various vibrational levels investigated in the literature, as again discussed by Thornley and Hutson.[4]

Local perturbations occur, which do affect the more regular structures detailed in section 6. They are usually observed in one branch only, because the corresponding R/P lines are obscured by overlapping lines or are too weak to be observed. The intensity in some of the branches actually falls off much more quickly than in others, probably revealing local Coriolis-type perturbation. Similar perturbations were reported in the ν_3, lower energy range,[5,21] and also left unassigned.

The relative line intensities were investigated in all assigned $R/Q/P$ series from the surface measured under a Voigt profile. Their evolution within a branch, averaged over all branches but one, converged toward a 9 K rotational temperature. Using this temperature to constrain the Doppler broadening, we determined the mean Lorentzian full-width to be 7×10^{-4} cm^{-1}. It corresponds to a mean half-time around 7.5 ns, to be compared to the close value of 11 ns determined for ν_3 in ref 5. Some lines show broader profiles, probably indicating either faster predissociation or more efficient intramolecular vibrational redistribution through local connections to the manifold of close dark states. This is actually the case, systematically, for all lines

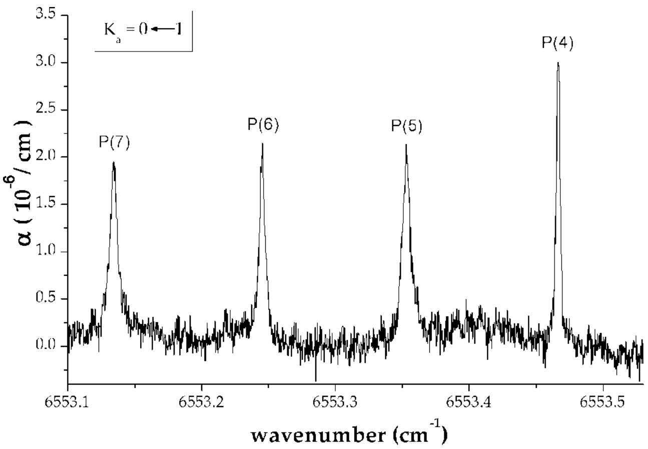

Figure 6. Example of anomalously large line broadening observed in the $K_a = 0 \leftarrow 1$ sub-band of the 2CH band of the $^{12}C_2H_2$−Ar van der Waals complex.

TABLE 4: Anomalous Lorentzian Full-Widths Measured for Lines in the $K_a = 0 \leftarrow 1$ Sub-Band of the 2CH Vibrational Band of the $^{12}C_2H_2$−Ar van der Waals Complex

J′	P(J)	Lorentz fwhm (MHz)	Q(J)	Lorentz fwhm (MHz)	R(J)	Lorentz fwhm (MHz)
0	P(1)	[a]				
1	P(2)	68	Q(1)	69		
2	P(3)	63	Q(2)	68	R(1)	[a]
3	P(4)	73	Q(3)	77	R(2)	72
4	P(5)	192	Q(4)	196	R(3)	156
5	P(6)	143	Q(5)	139	R(4)	141
6	P(7)	178	Q(6)	181	R(5)	[a]
7	P(8)	111	Q(7)	117	R(6)	119
8	P(9)	75			R(7)	70
9	P(10)	48			R(8)	61
10	P(11)	83			R(9)	88

[a] Overlapped.

within the $K_a = 0 \leftarrow 1$ sub-band. They indeed present a broader profile exemplified in Figure 6 for some lines. The corresponding, anomalous Lorentzian full-widths are listed for all lines in the sub-band in Table 4. They show very good agreement for all lines reaching the same upper *J* state in the $K = 0$ substate. A similar behavior was observed for a few lines around ν_3 by Miller and co-workers but is not further discussed in that paper.[5] Faster intramolecular vibrational redistribution could occur through local connections to the manifold of close dark states, probably induced by Coriolis-type mechanism. In any case, the acetylene−Ar van der Waals complex appears to be still well-bonded even at 1.5 μm vibrational excitation energy.

As a last comment concerning line profiles, it is interesting to point out that the *P*(9) to *P*(11) and *R*(7) to *R*(9) line positions in the $K_a = 0 \leftarrow 1$ sub-band do not match the ground-state combination differences as predicted from the rigid asymmetric top Hamiltonian constants. This behavior reveals some problem in the ground state, possibly due to the increased floppy character of the species at such high *J*-values. None of these levels were actually reported in the previous literature. We nevertheless assigned these lines as such because they all present very consistent, anomalously large Lorentzian profiles, as listed in Table 4. Their fwhm seems to be characteristic of the upper *J* state in the transition, as further supported by the consistency with the corresponding *Q*(J) fwhm. Their assignment is thus based on their specific fwhm, which is a quite unusual criterion. It obviously remains very tentative.

Additional, weaker series of lines are observed that present intensity dependence upon experimental conditions similar to the main sub-bands considered in section 3. Their carrier is thus tentatively identified to acetylene−Ar. This is the case for series of lines observed around 6550.8 and 6558.2 cm^{-1} and for less structured, denser spectral features arising between 6560.7 and 6564 cm^{-1}. Various assignments were considered, unsuccessfully, in terms of additional *K* sub-bands, hot bands, and contribution from other vibrational bands in acetylene. Furthermore, none of them could be rotationally analyzed either, in the higher energy range, because of the lack of regular structure, or, for the other series, because too few lines are observed.

6. Conclusion

We have further investigated the acetylene−Ar complex, using ab initio calculations and overtone spectroscopy. We first checked that the structure of the monomer is not significantly affected by complexation and that the calculated properties of the complex seem not to be very sensitive to the structure selected for the acetylene unit, as assumed in the previous literature. We then reported on high-resolution spectroscopic information in the $\nu_1 + \nu_3$ (2CH) vibrational state around 1.5 μm. The lifetime of the complex appears to be as long as 7.5 ns in this state, as resulting from the recorded Lorentzian linewidths. Rotational constants were obtained from the conventional analysis of the $K_a = 0 \leftarrow 1$, $1 \leftarrow 0$, and $2 \leftarrow 1$ sub-bands. Evidence on the floppy character of the complex in this overtone vibrational state resulted from the spectral analysis, for example from the inverted *K*-splitting observed for the upper levels with *J*, $K_a = 2$, K_c, and from anomalous linewidths. Several weaker series of lines and local perturbations remain to be assigned.

New, additional information was thus obtained on the acetylene−Ar prototype van der Waals complex, confirming previous literature results, and opening new issues concerning the overtone range, in which the complex appears to be stable enough to demonstrate resolved vibration−rotation structures.

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