

Nov, 12

Observation of the C₂H₂-N₂O van der Waals complex in the overtone range using CW-CRDS

To be submitted to Chemical Physics Letters

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Abstract

A slit nozzle supersonic expansion containing acetylene (0.246l/min) and nitrous oxide (0.355l/min) seeded into Ar (1.26l/min) is investigated using CW cavity ring down spectroscopy, in the 1.5 μm range. The $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ van der Waals complex is observed around the 2CH acetylenic band. Despite strong perturbations, 117 b-type lines are assigned. Their combined fit with published microwave data leads to new upper state and improved lower state rotational constants. The Lorentzian width of the assigned line profiles sets the mean lifetime to 1.6 ns. The rotational temperature is estimated to be 15K from the comparison between observed and simulated spectra.

1. Introduction

The structural information concerning the acetylene–nitrous oxide van- der Waals complex was retrieved in the 90’s from a limited number of high resolution spectroscopic investigation (1-4). The initial work was performed in the infrared range, dealing with the ν_3 , asymmetric stretch acetylenic band (1). After a first set of microwave data (2,3), a systematic analysis of various isotopic spectra (4) definitely confirmed that the complex is planar, with parallel monomer axes making roughly right angles with the vector connecting the monomer centres of mass. Following similar investigation of acetylene–Ar (5,6) and of acetylene multimers (7), we have

recorded spectra of $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ around $1.5\text{ }\mu\text{m}$, thus in the overtone range around the 2CH or $\nu_1+\nu_3$ acetylenic band, with mode 1 the symmetric CH stretching vibration and mode 3 previously defined.

2. Experimental procedure

The *FANTASIO* set-up, for “Fourier trANsform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansION”, was used (8). It 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). Gases were injected through a brass slit nozzle ($\sim 20 \times 0.5\text{ mm}$). Optimal conditions were found to be $P_{\text{in}} = 0.173\text{ hPa}$ (0.013 torr) (reservoir), $P_{\text{out}} = 1033\text{ hPa}$ (775 torr) (residual), and injection flows of 0.355 l/min for N_2O , 0.246 l/min for C_2H_2 , and 1.26 l/min for Ar, all from high purity commercial bottles. These conditions were measured using, respectively, MKS Baratron gauges (1333 and 1.33 hPa (1000 and 1 torr)) full scale, respectively) and MKS and Brooks flowmeters (10000 and 30000 sccm full scale, respectively).

The details of the CW cavity ring down spectrometer (CW-CRDS) are similar to those presented in previous descriptions of the set-up (5-8), and not repeated here. One only needs to recall that some 100 ring-downs per spectral point are fitted and their mean characteristic decay frequency (ν) is recorded.

The cavity is made of two concave mirrors (Radius = 1000 mm; Reflectivity = 99.988%), separated by about 540 mm. In the present case, the typical ring-down time was about 20 μ s, corresponding to some 11103 passes, *i.e.* about 220 m effective absorption pathlength in the jet-cooled molecules when using the present, 2 cm slit nozzle. Finally, tubes were set on the laser path in between the cavity mirror and the expansion, with a gentle flow of nitrogen to limit absorption from residual gas.

The line wavenumber measurement procedure was based on acetylene monomer lines as references (9). The measurement precision and accuracy are estimated to 5×10^{-4} and 10^{-3} cm^{-1} , respectively.

Various series of lines were identified in the spectra according to their intensity behaviour relative to the experimental conditions, some likely to arise from acetylene multimers (7), other from acetylene-Ar (5,6). We only consider in the next sections those lines that disappeared from the spectrum when removing either acetylene or nitrous oxide from the injected gases.

Finally, one should also mention unsuccessful attempts to observe the dimer around the $3\nu_3$ band of N_2O , at 6580.8 cm^{-1} (10), this band being still within the range of the available laser diodes, but of reduced strength compared to $\nu_1 + \nu_3$, C_2H_2 .

3. Results

The $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ complex can have either a/b-type hybrid bands or c-type bands if the vibrational mode is out-of-plane. There is no strong central Q-branch observed which rules out c-type transitions. In addition, there is no evidence of an a-type Q-branch at the band center either which would be expected since the microwave spectroscopy (2-4) studies indicate that the two monomer units are nearly parallel. A b-type band has a distinctive center with the ${}^{\text{r}}\text{Q}_0$ ($\Delta J = 0$, $\Delta K_{\text{a}} = +1$, $\Delta K_{\text{c}} = -1$) and ${}^{\text{p}}\text{Q}_1$ ($\Delta J = 0$, $\Delta K_{\text{a}} = -1$, $\Delta K_{\text{c}} = +1$) branches degrading to higher and lower frequencies respectively leaving a gap at the center of the band. This region was easily located and can be seen in Fig. 1. Unfortunately the spectrum is perturbed as one would expect in an overtone region with a high density of states; note that the $J=2$ transition in the ${}^{\text{r}}\text{Q}_0$ -branch is missing – no doubt the result of a crossing. Since the ground state constants were known from the work of Leung *et al.* (2-4) the assignment could be extended to higher K values. There appears to be an energy level crossing around the $K_{\text{a}} = 10, 11$, and 12 levels, and no transitions involving these energy levels could be assigned with confidence. However, a number of the upper state $K_{\text{a}} = 13$ transitions both in the P- and R-branches could be assigned with the aid of ground state combination differences even though these levels were badly perturbed. Altogether, some 117 lines were assigned, whose list can be obtained from the authors.

The ground state combination differences obtained were combined with the microwave data to obtain a slightly improved set of ground state constants. The “unperturbed” transitions were fit to type A Ir Watson Hamiltonian in order to obtain a set of upper state constants. Because of the perturbations, these constants must be regarded as empirical fitting parameters. Both upper state and ground state constants obtained are listed in Table 1. The assigned “unperturbed” infrared line wavenumbers are reproduced within $\sigma = 0.0028 \text{ cm}^{-1}$ using these constants. The band origin (6549.91 cm^{-1}) appears to be red shifted by as much as 6.55 cm^{-1} in the dimer compared to the acetylene monomer (11).

The constants from Table 1 were used to simulate the spectral range presented in Fig.1. The temperature was adjusted to 15K in the simulation to ensure optimal comparison with the observed spectrum.

Using this temperature to constrain the Doppler broadening, we determined the mean Lorentzian full-width to be $1.5 \times 10^{-4} \text{ cm}^{-1}$ for all assigned lines. It corresponds to a mean half-time around 1.6 ns, which is significantly shorter than for acetylene-Ar (7.5 ns) in the similar 2CH upper state (6).

Eventually one should mention that the present assignments only concern a small fraction, roughly **20%** of the observed lines. We were

unfortunately unable to extract any band structure out of the remaining lines. The fact that new branches could not be assigned using the present ground state rotational constants probably indicates that they are not additional combination or overtone bands in $\text{C}_2\text{H}_2\text{-N}_2\text{O}$. They are rather likely to be hot bands involving unidentified, low frequency intermolecular vibrations. The assignment of the additional lines to another geometrical structure of the dimer than planar with parallel monomer axes, as recently evidenced for pure N_2O (12) and OCS (13) complexes, cannot be excluded but would require reliable rotational assignments and/or *ab initio* predictions to be further assessed.

4. Conclusion

In conclusion, we have observed the $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ van der Waals complex with planar geometry and parallel monomer axes, around the $\nu_1+\nu_3$ acetylene band. This is the first report of overtone spectra in this species. Upper state rotational constants were obtained from the rotational analysis of unperturbed sub-bands. The assignment of the higher-K perturbed states remains a challenge in this highly excited vibrational range.

The present results set the dissociative lifetime of acetylene-nitrous oxide with planar geometry and parallel monomer axes to some 1.6 ns in the probed acetylenic, $\nu_1+\nu_3$ upper state. The $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ van der Waals complex

thus remains stable at such high vibrational excitation energy, as already reported for $\text{C}_2\text{H}_2\text{-Ar}$ (5,6) and $(\text{C}_2\text{H}_2)_2$ (7), as well as for non acetylene-containing complexes such as HF-Ar (14,15), $(\text{HF})_2$ (16-19), $(\text{HCN})_2$ (20), $(\text{H}_2\text{O})_2$ (21) and $(\text{N}_2\text{O})_2$ (22).

Acknowledgments

We are indebted to A. Rizopoulos (ULB) for helping during the experiments and to S. Robert (ULB) for identifying acetylene monomer lines. PM thanks FNRS and KD thanks FRIA for financial support. This work was sponsored by the Fonds National de la Recherche Scientifique (FNRS, contracts FRFC and IISN), the « Action de Recherches Concertées de la Communauté française de Belgique ». It is performed within the activities of the “LEA HiRes “. We thank Helen Leung of Amherst College for sending us her microwave transitions corrected for the nitrogen quadrupole splitting.

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Figure captions

Figure 1: A portion of the $\text{C}_2\text{H}_2\text{--N}_2\text{O}$ band near the band center showing a comparison of calculated ($T_{\text{rot}} = 15$ K) versus observed spectra. Two well resolved Q-branches are observed; the ${}^{\text{r}}\text{Q}_0$ transitions ($\Delta J = 0, \Delta K_a = +1, \Delta K_c = -1$) and the ${}^{\text{p}}\text{Q}_1$ transitions ($\Delta J = 0, \Delta K_a = -1, \Delta K_c = +1$). Note the $J = 2$ lines is missing from the ${}^{\text{r}}\text{Q}_0$ series due to a perturbation. The ${}^{\text{r}}\text{Q}_1$ series is also shifted due to a perturbation. The strong lines are from the monomer in the expansion, with lines labeled a: ${}^{12}\text{C}_2\text{H}_2$ $\text{P}_e(3)$, $\nu_1+\nu_3$; b: ${}^{13}\text{C}{}^{12}\text{CH}_2$ $\text{R}_e(2)$, $\nu_1+\nu_3$; c: ${}^{12}\text{C}_2\text{H}_2$ $\text{R}_e(8)$, $\nu_1+\nu_3+\nu_4-\nu_4$; d: ${}^{12}\text{C}_2\text{H}_2$ $\text{R}_f(8)$, $\nu_1+\nu_3+\nu_4-\nu_4$; e: ${}^{12}\text{C}_2\text{H}_2$ $\text{R}_e(6)$ $\nu_1+\nu_3+\nu_5-\nu_5$.

Figure 2: A small section of the R-branch of the $\text{C}_2\text{H}_2\text{---N}_2\text{O}$ band. The labeled transitions are definitely assigned. The unlabeled lines are either shifted by the strong perturbation or lines of another band.

Table legends

Table 1: Spectroscopic fitting constants obtained for the $\text{C}_2\text{H}_2\text{--N}_2\text{O}$ dimer (cm^{-1}).

Table 1

	Ground state	Upper state
A	0.313359399(48) ^a	0.31589(11)
B	0.09446473(11)	0.094033(41)
C	0.07231532(17)	0.072540(44)
$\delta_J \times 10^6$	0.11226(23)	0.538(76)
$\delta_K \times 10^5$	0.2036(87)	102.(12)
$h_K \times 10^5$	-	0.128(12)
$\Delta_K \times 10^6$	0.825(46)	538.7(48)
$\Delta_{JK} \times 10^5$	0.1603(15)	-40.84(11)
$\Delta_J \times 10^6$	0.4585(20)	8.74(14)
$H_K \times 10^6$	-	0.345(60)
$L_K \times 10^8$	-	0.169(22)
v_0^0		6549.91374(87)

^a Uncertainties are 1 standard deviation.

Figure 1

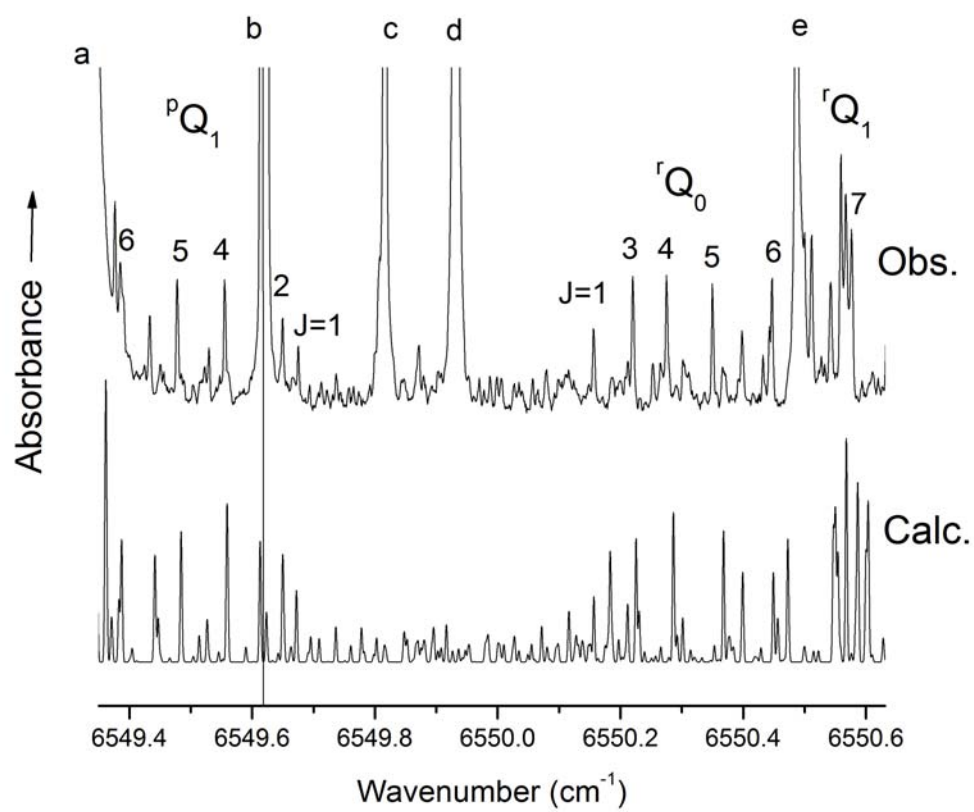


Figure 2.

