

The millimeter-wave spectrum and the dipole moment of vinylacetylene^{*}

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Abstract. The pure rotational spectrum of the hydrocarbon vinylacetylene (1-butene-3-yne, $\text{H}_2\text{C} = \text{CH} - \text{C} \equiv \text{CH}$) in its ground vibrational state has been investigated from 80 to 165 GHz, covering the rotational quantum numbers $8 \leq J \leq 18$ and $0 \leq K_a \leq 17$, in order to provide accurate rest frequencies for radioastronomical searches. Moreover, quantum chemical calculations of the dipole moment components μ_a and μ_b have been performed leading to the result $\mu_a \approx 0.4$ D. The value for the dipole moment component μ_b is very low and lies in the range of several thousandth to a few hundredth of a Debye.

Key words. molecular data – methods: laboratory – techniques: spectroscopic – stars: AGB and post-AGB

1. Introduction

Recent astrochemical modelling has shown that the pure hydrocarbon vinylacetylene (VA) supposedly is a very abundant molecule in circumstellar shells of late type stars (Cernicharo 2002). To date, laboratory studies of the pure rotational spectrum of VA were reported by Morgan & Goldstein (1952), Hirose (1970) and Tørneng et al. (1980). However, none of these investigations extended to frequencies above 37 GHz, complicating a targeted radioastronomical search for the molecule in the millimeter-wave region.

In this *Letter*, we report the investigation of the pure rotational spectrum of VA from 80 to 165 GHz corresponding to wavelengths of 3 and 2 mm, respectively. Moreover, quantum chemical calculations of the dipole moment have been performed.

2. Experimental

Vinylacetylene was synthesized by di-dehydrochlorination of 1,4-dichloro-2-butene as described by Tørneng et al. (1980).

The millimeter wave spectrum of VA was recorded employing a commercial spectrometer (AM-MSP series, Analytik & Meßtechnik GmbH, Chemnitz), whose detailed description is given elsewhere (Winnewisser et al. 2000). Briefly, millimeter wave radiation is generated by a continuously tunable backward wave oscillator (BWO) which is phase-locked to a

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^{*} Table 1 is only available in electronic at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via <http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/398/L11>

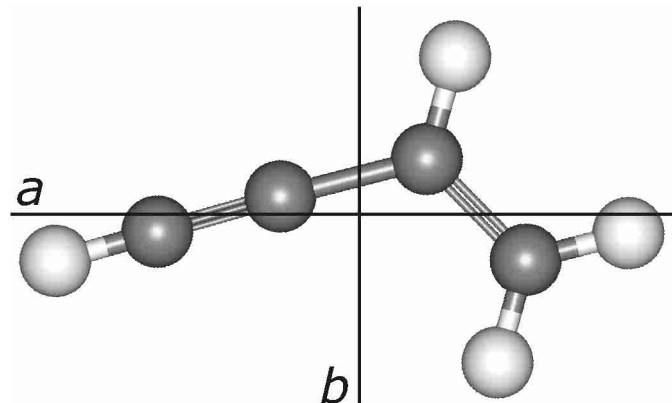


Fig. 1. The molecular structure of vinylacetylene along with the a and b principle axes of inertia. Carbon atoms are shown in grey whereas hydrogen atoms are shown in white.

reference signal provided by a frequency generator operating from 4.0 to 5.4 GHz. A Schottky-barrier diode operating at room temperature is used as a detector. Source frequency modulation and $2f$ harmonic detection is employed so that the second derivative of the actual absorption signal is recorded.

3. Analysis

The molecular structure of VA is shown in Fig. 1. VA is a prolate near-symmetric top molecule with a value of $\kappa = (2B - A - C)/(A - C) = -0.98$ for Ray's asymmetry parameter which is very close to the value of -1 for the limiting prolate symmetric top. The structure gives rise to two dipole moment components μ_a and μ_b , the stronger of which is along the a -axis

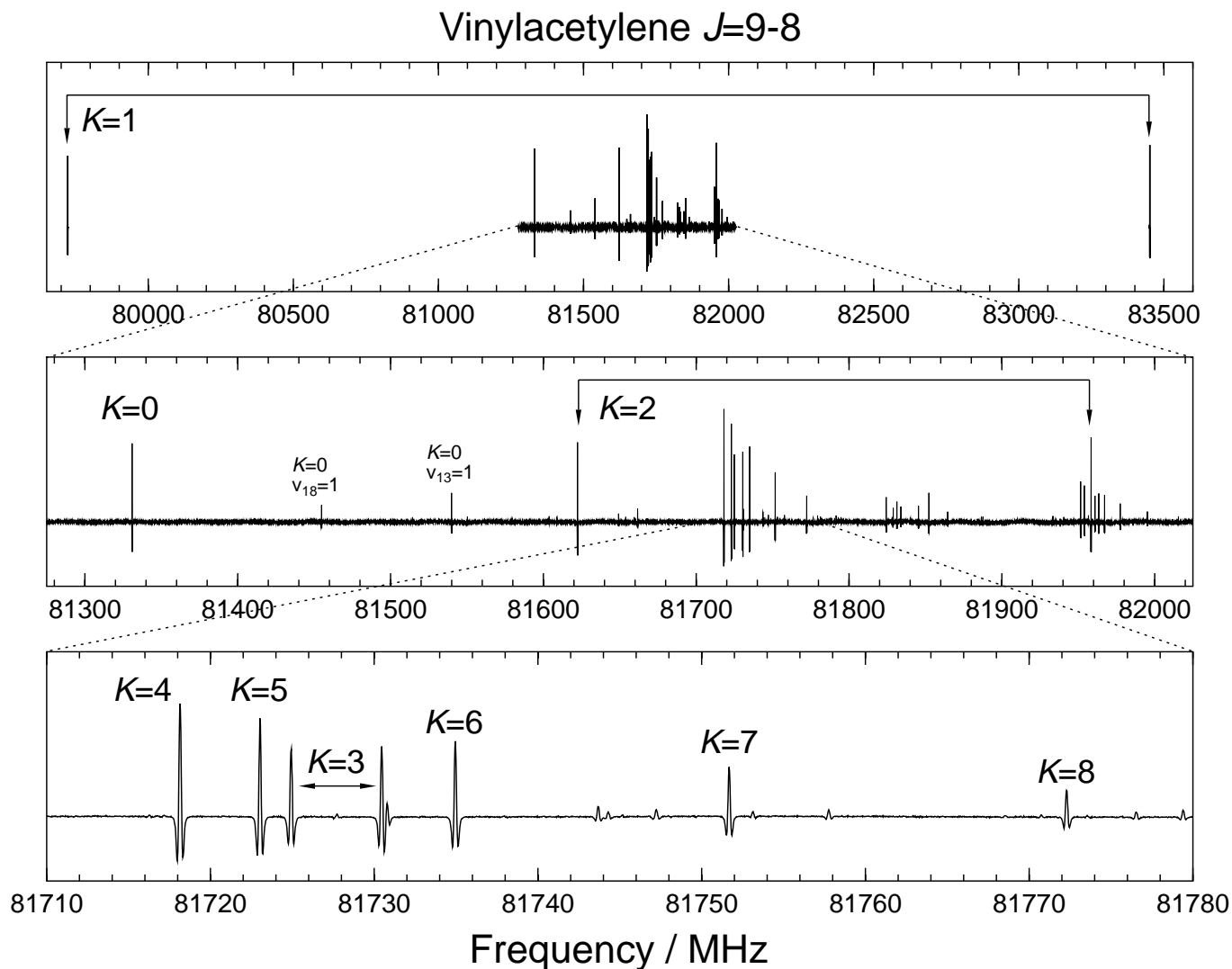


Fig. 2. Laboratory survey spectrum of the $J = 9 - 8$ transition of vinylacetylene at 82 GHz ($K = K_a$). The upper trace shows the entire rotational transition dominated by the asymmetry splitting of the $K = 1$ lines. The center trace shows a spectrum from 81.3 to 82.0 GHz and the lower trace shows a detail of the spectrum highlighting the transitions with $K = 3$ to $K = 8$. The strong spectroscopic features have been assigned. The majority of the remaining weaker lines is due to vibrationally excited states of vinylacetylene.

of the molecule roughly aligned to the carbon backbone (cf. Fig. 1). In the present investigation, a total of 119 pure rotational a -type transitions of VA has been recorded (unresolved asymmetry doublets only counted once) from 80 to 165 GHz (3 and 2 mm region). An example spectrum in the 3 mm regime is shown in Fig. 2. In addition to strong R -branch transitions, weaker Q -branch transitions with $1 \leq K_a \leq 3$ have been observed. The entire set of transition frequencies is given in Table 1 which is available in electronic form at the CDS. The transition frequencies have been fitted employing Pickett's program SPFIT (Pickett 1991) using a Watson-type Hamiltonian in the S reduction and under consideration of the previously published data (Hirose 1970; Tørneng et al. 1980). The new set of molecular parameters is shown in Table 2. As can be seen, a comprehensive set of molecular parameters has been determined including the full set of quartic as well as additional sextic and octic centrifugal distortion constants. The weighted rms of 0.55 demonstrates that the experimental transition

frequencies are very well reproduced within the estimated experimental uncertainties. Moreover, the high quality of the fit is revealed by the small residuals ($obs - calc$) given in Table 1. The present set of molecular parameters thus allows for the accurate calculation of the entire microwave- and millimeter-wave spectrum of VA in its ground vibrational state.

4. The dipole moment of vinylacetylene

So far, two experimental investigations of the dipole moment of VA have been reported in the literature: while Sobolev et al. (1962) found an a -type dipole moment component μ_a of 0.43 (1) D, a later study by Hirose (1970) yielded a value of 0.223 (2) D, lower by almost exactly a factor of two. Since the exact knowledge of this dipole moment component will be crucial for calculating column densities or upper limits for the abundance of VA from radioastronomical data, this discrepancy

Table 2. Molecular parameters of vinylacetylene (MHz).

Parameter	Value
<i>A</i>	50 300.158 (55)
<i>B</i>	4 744.942 54 (22)
<i>C</i>	4 329.773 04 (23)
<i>D_J</i> × 10 ³	1.821 61 (87)
<i>D_{JK}</i> × 10 ³	−83.253 8 (23)
<i>D_K</i>	3.290 9 (83)
<i>d₁</i> × 10 ³	−0.386 82 (15)
<i>d₂</i> × 10 ⁶	−27.162 (92)
<i>H_J</i> × 10 ⁹	4.3 (14)
<i>H_{JK}</i> × 10 ⁶	−0.318 5 (34)
<i>H_{KJ}</i> × 10 ⁶	−5.990 (22)
<i>H_K</i> × 10 ³	0.4 ^a
<i>h₁</i> × 10 ⁹	2.182 (30)
<i>L_{KKJ}</i> × 10 ⁹	0.638 (64)
wrms ^b	0.55

^a Kept fixed in the fit.^b Weighted rms (dimensionless).**Table 3.** Dipole moment components μ_a and μ_b of vinylacetylene (D). The values have been obtained based on a structure optimized at the CCSD(T)/cc-pVTZ level of theory.

	μ_a		μ_b	
	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ
MP2	0.3660	0.3771	0.0105	0.0054
BLYP	0.3909	0.4043	0.0331	0.0277
BPW91	0.4092	0.4165	0.0203	0.0159
B3LYP	0.4341	0.4446	0.0160	0.0103
B3PW91	0.4471	0.4535	0.0061	0.0014

prompted us to perform an ab initio study presented in the following.

The equilibrium geometry of VA was optimized at the CCSD(T)/cc-pVTZ level of theory, with all electrons included in the correlation treatment. Upon that basis, the two dipole moment components μ_a and μ_b have been calculated employing second order Møller-Plesset perturbation theory (MP2) as well as various density functional methods (BLYP, BPW91, B3LYP, B3PW91, cf. Table 3). In order to make sure that the calculated dipole moments are not significantly affected by too small a basis set, these calculations have been performed with both the cc-pVTZ and the larger cc-pVQZ basis set. For all calculations, the Gaussian 98 program package (Frisch et al. 1998) has been used. As can be seen from Table 3, the values for the dipole moment component μ_a calculated with the cc-pVTZ basis set range from 0.366 to 0.447 D, while those calculated with the cc-pVQZ basis set are only marginally higher. Thus, our results strongly speak in favor of the work of Sobolev et al. (1962).

In addition, from the calculations it is concluded that the dipole moment component μ_b is most likely smaller by more than a factor of 10, and probably even by more than a factor of 100.

5. Discussion

The millimeter-wave spectrum of vinylacetylene in the ground vibrational state has been investigated to yield a comprehensive set of rotational and centrifugal distortion constants that will aid a targeted search for that molecule in space. Moreover, the dipole moment has been determined by means of quantum chemical calculations.

Frequency predictions for vinylacetylene based on the present investigation can be found online in the Cologne Database for Molecular Spectroscopy (CDMS, Müller et al. 2001) at <http://www.cdms.de>.

Since bending fundamentals of VA are of very low energy they are easily excited. As can be seen in Fig. 2, the spectrum shows a plethora of vibrational satellites especially appendant to the two lowest bending modes ν_{13} and ν_{18} at 225 and 305 cm^{−1} as well as their combination mode and overtones. Work on the millimeter-wave spectrum of VA in vibrationally excited states as well as on its submillimeter-wave spectrum is currently in progress.

Finally, it might be pointed out that the astronomical detection of the related and isoelectronic molecule vinyl cyanide, H₂C = CH – CN, marked the first discovery of a C = C double bond in space (Gardner & Winnewisser 1975). Since these days, vinyl cyanide in its ground vibrational state has been found in many interstellar sources. Additionally, it has also been detected in vibrationally excited states in several star forming regions (e.g. Nummelin & Bergman 1999).

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