

Infrared Spectra of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$: The ν_5^1 Band

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The infrared absorption lines of a mixture of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$ around 725 cm^{-1} have been recorded with a high resolution (0.04 cm^{-1}) FTIR spectrometer. Rotational structures of P , R and Q branches of the ν_5^1 bands were analyzed and molecular constants ν_0 , B' , B'' , D' and D'' calculated.

Introduction

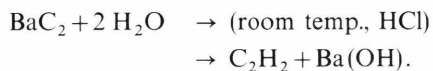
Although a very large number of papers on the high resolution infrared spectrum of acetylene and its deuterated species were published in recent years, the spectra of isotopic carbon species received comparatively little attention. The first paper reporting investigations of $^{12}\text{C}^{13}\text{CH}_2$ and $^{13}\text{C}_2\text{H}_2$ was published by Lafferty and Thibault and it was based on spectra recorded in the near infrared region ($\sim 2600\text{ cm}^{-1}$), indirectly yielding rotational constants for ν_5^1 , as well as ν_3 [1]. Scott and Rao recorded for the first time the ν_5^1 band of $^{12}\text{C}^{13}\text{CH}_2$ [2]. Using tunable diode laser, Das et al. recorded several Q branch lines of the $2\nu_5^0 - \nu_5^1$ band of $^{12}\text{C}^{13}\text{CH}_2$ and $^{13}\text{C}_2\text{H}_2$ calculating high precision molecular constants for the ν_5^1 and $2\nu_5^0$ states [3].

For $^{14}\text{C}_2\text{H}_2$ only one medium resolution (0.3 cm^{-1}) infrared measurement recorded by Mink and Kemény is known, with a preliminary vibrational analysis of ν_3 , $\nu_4 + \nu_5^1$ and ν_5^1 bands. In an attempt to determine molecular constants, these authors encountered some difficulties due to the insufficient accuracy of their measurements [4].

The prime object of the current investigation is to record the infrared spectrum of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$ under high resolution. This article presents the observational results and the interpretation of the rotational structure of ν_5^1 band.

Experimental

^{14}C substituted acetylene gas was prepared by the following reaction:



Due to the relatively high ^{12}C content of the starting material of $\text{Ba}^{14}\text{CO}_3$, a mixture of about 3:2 of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$, some 5–7 percents of $^{14}\text{C}_2\text{H}_2$ and, as a by-product, $^{12,14}\text{C}_2\text{H}_6$ have been formed. The reaction was carried out in a special vacuum system, and the resulting gas was then dried and collected in a liquid nitrogen trap.

The infrared spectra were recorded on a Nicolet 170SX FTIR interferometer between 4000 and 400 cm^{-1} at a resolution of 0.04 cm^{-1} , in a 21 cm gas cell, using 30, 5 and 2 Torr pressures.

Results

In Fig. 1 details of the spectrum recorded at 2 Torr pressure are shown. Due to the presence of three main isotopic species ($^{14}\text{C}_2\text{H}_2$, $^{12}\text{C}^{14}\text{CH}_2$ and $^{12}\text{C}_2\text{H}_2$) of commensurable concentrations, and in addition to the high number of their different “hot” bands, the spectral bands were very often strongly confused by overlapping. Therefore, the assignments of relatively low intensity “hot” bands were complicated by the fact

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Band	$0000^0 1^- - 0000^0 0^0$ ($\Sigma_g^+ - \Pi_u$) of $^{14}\text{C}_2\text{H}_2$				(units in cm^{-1})			
J	obs.	calc.	o - c	weight	obs.	calc.	o - c	weight
R(J)					P(J)			
00	727.724	.723	.001	1.0000				
01	729.865	.858	.007	0.0006				
02	731.985	.991	-.006	0.0006	721.314	.315	-.001	1.0000
03	734.123	.124	-.001	1.0000	719.176	.178	-.002	1.0000
04	736.257	.257	.000	1.0000	717.036	.040	-.004	1.0000
05	738.394	.388	.006	1.0000	714.899	.902	-.003	1.0000
06	740.524	.519	.005	1.0000	712.763	.763	.000	1.0000
07	742.647	.648	-.001	1.0000	710.620	.624	.004	1.0000
08	744.785	.777	.008	1.0000	708.482	.484	-.002	1.0000
09	746.900	.905	-.005	1.0000	706.340	.344	-.004	1.0000
10	749.033	.032	.001	1.0000	704.202	.204	-.002	1.0000
11	751.156	.157	-.001	1.0000	702.060	.063	-.003	1.0000
12	753.283	.282	.001	1.0000	699.922	.922	.000	1.0000
13	755.401	.406	-.005	1.0000	697.782	.780	.002	1.0000
14	757.534	.528	.006	1.0000	695.643	.638	.005	1.0000
15	759.646	.649	-.003	1.0000	693.501	.496	.005	1.0000
16	761.770	.769	.001	1.0000	691.363	.354	.009	0.0006
17	763.888	.888	.000	1.0000	689.223	.212	.011	0.0006
18	766.004	.005	-.001	1.0000	687.081	.070	.011	0.0006
19	768.115	.121	-.006	1.0000	684.932	.927	.005	1.0000
20	770.240	.236	.004	1.0000	682.781	.784	-.003	1.0000
21	772.356	.350	.006	1.0000	680.638	.642	-.004	1.0000
22	774.480	.462	.018	0.0006	678.497	.499	-.002	1.0000
23	776.575	.572	.003	1.0000	676.357	.356	.001	1.0000
24	778.684	.681	.003	1.0000	674.215	.213	.002	1.0000
25	780.787	.788	-.001	1.0000	672.078	.071	.007	1.0000
26	782.897	.894	.003	1.0000	669.928	.928	.000	1.0000
27	784.997	.999	-.002	1.0000	667.790	.786	.004	1.0000
28	787.097	.101	-.004	1.0000	665.648	.644	.004	1.0000
29	789.203	.202	.001	1.0000	663.502	.502	.000	1.0000
30	791.299	.301	-.002	1.0000	661.352	.360	-.008	0.0006
31	793.393	.398	-.005	1.0000	659.214	.218	-.004	1.0000
32	795.495	.494	.001	1.0000	657.072	.077	-.005	1.0000
33	797.582	.588	-.006	1.0000	654.931	.936	-.005	1.0000
34	799.682	.680	.002	1.0000	652.792	.795	-.003	1.0000
35	801.766	.769	-.003	1.0000	650.653	.654	-.001	1.0000
36	803.851	.857	-.006	1.0000	648.514	.514	.000	1.0000
37	805.946	.943	.003	1.0000	646.375	.374	.001	1.0000
38	808.032	.027	.005	1.0000	644.241	.235	.006	1.0000
39	810.112	.109	.003	1.0000	642.096	.096	.000	1.0000
40	812.163	.189	-.026	0.0006	639.960	.958	.002	1.0000
41	814.270	.266	.004	1.0000	637.818	.820	-.002	1.0000
42	816.348	.342	.006	1.0000	635.682	.683	-.001	1.0000
43	818.412	.415	-.003	1.0000	633.565	.546	.019	0.0006
44	820.483	.485	-.002	1.0000				
45	822.554	.554	.000	1.0000				
46	824.614	.620	-.006	1.0000				
47	826.687	.684	.003	1.0000				
					Standard deviation .00037			

Band	$0000^0 1^- - 0000^0 0^0$ ($\Sigma_g^+ - \Pi_u$) of $^{12}\text{C}^{14}\text{CH}_2$				(units in cm^{-1})			
J	obs.	calc.	o - c	weight	obs.	calc.	o - c	weight
R(J)					P(J)			
00	729.740	.739	.001	1.0000				
01	731.985	.985	.000	1.0000	725.240	.246	-.006	1.0000
02	734.236	.230	.006	1.0000	722.998	.998	.000	1.0000
03	736.472	.475	-.003	1.0000	720.745	.750	-.005	1.0000
04	738.725	.719	.006	1.0000	718.506	.502	.004	1.0000
05	740.962	.963	-.001	1.0000	716.253	.253	.000	1.0000
06	743.212	.205	.007	1.0000	714.004	.004	.000	1.0000
07	745.447	.447	.000	1.0000	711.758	.754	.004	1.0000
08	747.683	.688	-.005	1.0000	709.503	.504	-.001	1.0000
09	749.935	.928	-.007	1.0000	707.253	.254	-.001	1.0000
10	752.168	.168	.000	1.0000	705.006	.754	.002	1.0000
11	754.403	.406	-.003	1.0000	702.752	.754	-.002	1.0000
12	756.645	.643	.002	1.0000	700.498	.503	-.005	1.0000
13	758.885	.880	.005	1.0000	698.256	.252	.004	1.0000
14	761.118	.115	.003	1.0000	696.003	.002	.001	1.0000
15	763.348	.349	-.001	1.0000	693.744	.751	-.007	1.0000
16	765.578	.583	-.005	1.0000	691.495	.500	-.005	0.0006
17	767.810	.815	-.005	1.0000	689.223	.249	-.026	0.0001
18	770.042	.045	-.003	1.0000	687.995	.998	-.003	1.0000
19	772.270	.275	-.005	1.0000	684.747	.748	.001	1.0000
20		4.503		0.0000	682.502	.497	.005	1.0000
21	776.726	.730	-.004	1.0000	680.245	.247	-.002	1.0000
22	778.957	.956	.001	1.0000	677.996	.996	.000	1.0000
23	781.187	.180	.007	1.0000	675.750	.746	.004	1.0000
24	783.408	.403	.005	1.0000	673.495	.496	-.001	1.0000
25	785.618	.624	-.006	1.0000	671.243	.247	-.004	1.0000
26	787.845	.844	.001	1.0000	669.003	8.997	.006	1.0000
27	790.070	.063	.007	1.0000	666.746	.748	-.002	1.0000
28	792.276	.279	-.003	1.0000	664.500	.500	.000	1.0000
29	794.498	.494	.004	1.0000	662.253	.252	.001	1.0000
30	796.705	.708	-.003	1.0000	660.000	.004	-.004	1.0000
31	798.918	.920	-.002	1.0000	657.763	.757	.006	1.0000
32	801.132	.129	.003	1.0000	655.505	.510	-.005	1.0000
33	803.334	.338	-.004	1.0000	653.270	.263	.007	1.0000
34	805.543	.544	-.001	1.0000	651.017	.017	.000	1.0000
35	807.747	.748	-.001	1.0000	648.777	.772	.005	1.0000
36	809.954	.951	.003	1.0000	646.525	.527	-.002	1.0000
37	812.160	.151	.009	0.0100		4.283		0.0000
38	814.350	.350	.000	1.0000	642.037	.040	-.003	1.0000
39	816.545	.546	-.001	1.0000		9.797		0.000
40	818.738	.741	-.003	1.0000	637.558	.555	.003	1.0000
41	820.932	.933	-.001	1.0000		5.314		0.0000
42	823.128	.123	.005	1.0000		3.073		0.0000
43		5.311		0.0000	630.830	.834	-.004	1.0000
	Standard deviation .00038							

that often only a limited number of adjacent J lines of a given series could be located, and hence they will be omitted here. On the other hand, complete series of the dominating ν_5^1 fundamental bands were assigned up to about $J=47$ for $^{14}\text{C}_2\text{H}_2$ and $J=43$ for $^{12}\text{C}^{14}\text{CH}_2$. As expected, the ν_5^1 band system, which is due to the transition $\Sigma_g^+ - \Pi_u$, showed for the symmetric species $^{14}\text{C}_2\text{H}_2$ the expected 3:1 alternating intensities in the P and R lines. For both isotopic species the Q branches were partly resolved by diode laser spectroscopy, as shown in Figure 2.

In order to determine the band centers and rotational constants, we used a least squares program to fit the experimental data using to the following standard expression:

$$\begin{aligned} v(J' - J'') = & v_0 + B'[J'(J'+1) - l'^2] - D'[J'(J'+1) - l'^2]^2 \\ & + H'[J'(J'+1) - l'^2]^3 - B''[J''(J''+1) - l''^2] \\ & + D''[J''(J''+1) - l''^2]^2 \\ & - H''[J''(J''+1) - l''^2]^3. \end{aligned} \quad (1)$$

Here $v_0 = G_0(v', l') - G_0(v'', l'')$ is the vibrational band origin, $l' = 0$ for the upper Σ state, $l'' = 1$ for the lower Π state, and the constants of the higher state refer to the e sublevels in the case of R and P transitions, while those of the lower state to the f sublevels at the $Q(J)$ lines. In the latter case, an unambiguous analysis was defined, due to the overlaps of Q lines by lines from other bands. Therefore we used in our calculations, instead of (1), the approximation

$$\begin{aligned} v(J) = & v_0 - B' - D' + (B' - B'') J(J+1) \\ & + (D' - D'') [J(J+1)]^2. \end{aligned} \quad (2)$$

In Table 1 we collected the observed frequencies of both P and R lines of $^{14}\text{C}_2\text{H}_2$, the differences between observed and calculated values and the weights used. Table 2 shows the respective data of $^{12}\text{C}^{14}\text{CH}_2$. The data concerning the $Q(J)$ branches of both isotopic species are collected in Table 3.

Concerning the accuracy of our measurements, the influence of the H constants was expected to be negligible also in the case of P and R branches. Calculating from the Q lines, even the $v_0 - B' - D'$ values (725.559(3) and 725.498(5), for $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$, respectively), and those of $B'_f - B''_f$ (0.003779(26) and 0.003946(33), respectively) may be considered as a rough estimate due to the uncertainties of about ± 1 in assignments to the J numbers, besides the difficulties involved by the overlaps as mentioned above.

Table 3.

Q Branch lines of the band $0000^01^1 - 0000^00^0$ ($\Sigma_g^+ - \Pi_u$) of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$ (units in cm^{-1}).

J	obs.	calc.	o - c	weight	obs.	calc.	o - c	weight
$^{14}\text{C}_2\text{H}_2$					$^{12}\text{C}^{14}\text{CH}_2$			
06	725.713	.717	-.004	1.0000	727.670	.664	.006	1.0000
07	725.773	.769	.004	1.0000	727.724	.720	.004	1.0000
08	725.829	.829	.000	1.0000	727.790	.783	.007	1.0000
09	725.893	.896	-.003	1.0000	727.853	.855	-.002	1.0000
10	725.983	.970	.013	1.0000	727.913	.935	-.022	1.0000
11	726.060	.051	.009	0.0100	728.015	.023	-.008	1.0000
12	726.135	.138	-.003	1.0000	728.122	.120	.002	1.0000
13	726.224	.233	-.009	1.0000	728.242	.225	.017	1.0000
14	726.338	.334	.004	1.0000	728.335	.338	-.003	1.0000
15	726.438	.442	-.004	1.0000	728.454	.460	-.006	1.0000
16	726.555	.556	-.001	1.0000	728.602	.590	.011	1.0000
17	726.678	.676	.002	1.0000	728.726	.730	-.004	1.0000
18	726.797	.803	-.006	1.0000	728.877	.878	-.001	1.0000
19	726.943	.935	.008	1.0000	729.028	.035	-.007	1.0000
20	727.070	.072	-.002	1.0000	729.198	.201	-.003	1.0000
21	727.217	.216	.001	1.0000	729.383	.376	.007	1.0000
22	727.368	.364	.004	1.0000		.561		0.0000
23		.517		0.0000		.755		0.0000
24	727.670	.676	-.006	1.0000	729.960	.959	.001	1.0000
25		7.838		0.0000	730.174	.172	.002	1.0000
26		8.005		0.0000		.395		0.0000
27		8.167		0.0000	730.626	.629	-.003	1.0000

Standard deviation	.006	.009
$B'_f - B''_f = .003779(26)$		$B'_f - B''_f = .003946(33)$
$D'_f - D''_f = -.00000042(4)$		$D'_f - D''_f = .00000026(4)$

The calculated band origin frequencies, band centers and molecular constants are summarized in Table 4, together with the respective data for $^{12}\text{C}_2\text{H}_2$, $^{13}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{13}\text{CH}_2$. It can be seen that the errors of our data are at the level of those for $^{12}\text{C}_2\text{H}_2$, reported by Palmer *et al.* [5], in accordance with an identical resolution of 0.04 cm^{-1} for both measurements.

However, the errors of the constants calculated for the f sublevels from the Q lines are in both cases similarly high, when comparing the band center frequency estimated from the Q branch by Palmer *et al.* ($729,1503 \text{ cm}^{-1}$) with that obtained with very high precision infrared tunable diode laser measurements by Das *et al.* ($729,15639(19) \text{ cm}^{-1}$ in [5]) or their considerably differing values of $B'_f = 1.181112(19)$ and $1.178768(23)$, respectively, which might be accounted for by an error in Palmer's assignment of the lines to the J numbers by ± 1 (or more). On the other hand,

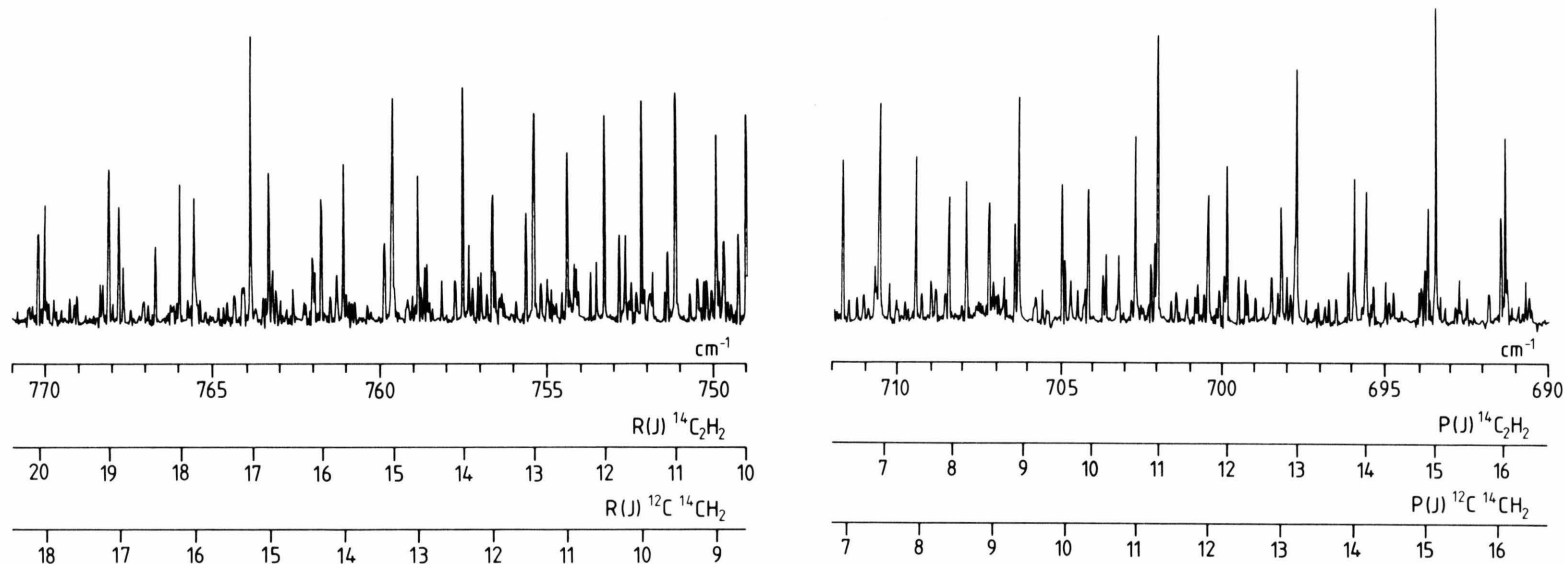


Fig. 1. Parts of the infrared spectrum of the mixture of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$ in the ν_5^1 region (recorded at 2 Torr). – The intensity alternation observed for the $^{14}\text{C}_2\text{H}_2$ is clearly seen for the P branch lines, whereas the R branch is more confused.

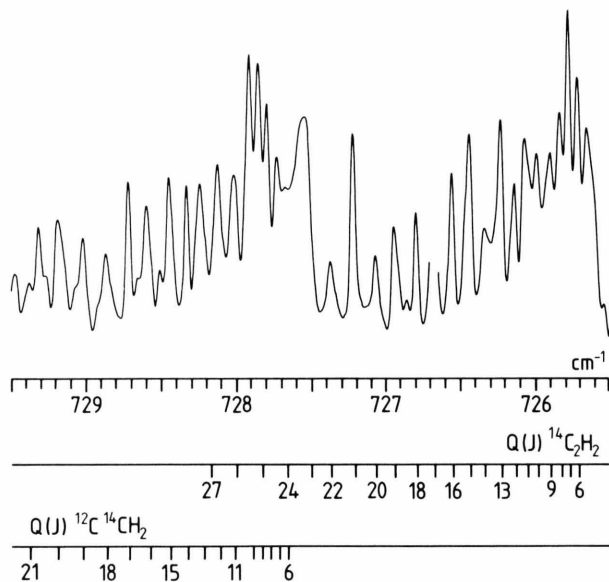


Fig. 2. Diode laser spectra of the Q branches of ν_5^1 of $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$.

Table 4. Spectroscopic constants for the $0000^0 1^1 - 0000^0 0^0$ ($\Sigma_g^+ - \Pi_u$) transitions of C_2H_2 (units in cm^{-1}).

Molecule	$\nu_0 = G'_0 - G''_0$	$\nu_0 - B' l'^2 + B'' l''^2$	B'	B''	$D' \times 10^6$	$D'' \times 10^6$	Ref.
$^{12}\text{C}_2\text{H}_2$	(e, f) 730.3314(16)	(e) 729.1550	(e) 1.176412(18)	1.176608(14)	1.610(9)	1.610(7)	[5]
		(f) 729.1503	(f) 1.181112(19)		1.655(10)		[5]
	(f) 730.33281(19)	(f) 729.15639(19)	(f) 1.178768(23)				[3]
$^{12}\text{C}^{13}\text{CH}_2$		(728.23) ^a		1.14840(2)		1.56(2)	[1]
$^{13}\text{C}_2\text{H}_2$		(726.98) ^a		1.11949(4)		1.47(2)	[1]
$^{12}\text{C}^{14}\text{CH}_2$	(e) 728.6156(7)	(e) 727.4926(7)	(e) 1.123267(20)	1.123533(20)	1.475(9)	1.467(9)	this work
		(f) 727.4980(48)	(f) 1.12748(4) ^b				
$^{14}\text{C}_2\text{H}_2$		(e) 725.5877(7)	(e) 1.067635(19)	1.067972(19)	1.366(7)	1.359(8)	this work
		(f) 725.5916(33)	(f) 1.07175(3) ^b				

^a Predicted value

^b Value estimated from $B'_f - B''_f$

the estimated values of constants B'_f , for $^{14}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{14}\text{CH}_2$, at this level of accuracy, seem to be realistic in comparison to that of $^{12}\text{C}_2\text{H}_2$.

In future we plan to measure highly precise diode laser spectra of selected hydrocarbons, including ^{14}C -isotopically substituted acetylene. Hydrocarbons have been discovered as constituents of planetary atmospheres. Their detailed assignment requires highly

accurate laboratory data sets, which we plan to provide with future diode laser work.

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