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Study of hot bands in the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system of C_2^- anion*

Yu Shan-Shan(喻姗姗)[a], Yang Xiao-Hua(杨晓华)[a], Li Ben-Xia(李本霞)[a], Kaniki Kakule[b], Wu Sheng-Hai(吴升海)[a], Guo Ying-Chun(郭迎春)[a], Liu Yu-Yan(刘煜炎)[a], and Chen Yang-Qin(陈扬骎)[c]†

[a] *Key Laboratory of Optical & Magnetic Resonance Spectroscopy, and Department of Physics, East China Normal University, Shanghai* 200062, *China*

[b] *University of Kinshasa, Faculty of Engineering, P.O. Box* 255 *Kinshasa* 11, *Dem. Rep. of Congo*

[c] *Department of Physics, East China Normal University, Shanghai* 200062, *China*

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Optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy was employed to observe the visible absorption spectra of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ electronic transition of C_2^-. Four hot bands (0,1), (1,2), (2,3) and (3,4) have been observed and the band (3,4) is measured directly for the first time, so far as we know, by absorption. A rotational analysis was carried out to obtain molecular constants. With the Franck–Condon principle and the vibrational Boltzmann distribution, we have estimated the vibrational temperature of C_2^- to be about 3000K.

Keywords: C_2^- anion, velocity modulation spectroscopy, vibrational temperature
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1. Introduction

During the last 25 years, negative molecular ions had been received more and more attention. However, their spectroscopic information is still extremely scarce due to insufficient concentration and inadequate purity of the negative ions generated in discharge. Conventional absorption or emission spectroscopic techniques are not suitable to obtain the spectrum of negative ions for their low sensitivity. A more serious difficulty is intrinsic to negative ions themselves. The lowest electronic excited states of negative ions have energies of at least several eV, while electron affinity, the amount of energy released when an electron is added to an atom, is typically less than 4eV, hence it is very difficult for bound electronic excited states to exist.

The diatomic carbon anion C_2^- is a very important negative molecular ion. It is one of a few gaseous molecular anions with bound electronic excited states. This special characteristic results from the high electron affinity of C_2 and the low electronic excited states of C_2^-. Vardya and Krishna Swamy[1] and Wallerstein[2] suggested that C_2^- might be a possible component in the atmosphere of carbon stars. Sarre[3] supposed that C_2^- might play an important role in the chemistry of interstellar medium. The electronic transition of C_2^-, both absorption and emission spectra in the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system, was first observed by Herzberg and Lagervist.[4] Nine bands, namely (0,0), (1,0), (0,1), (1,1), (1,2), (2,1), (2,3), (3,2) and (4,3), were observed and analysed. Due to the relatively low resolution ($0.2cm^{-1}$) of their experiments, they could not confirm the identification in the beginning until two-photon photodetachment of C_2^- was observed by Lineberger and Patterson[5] in a mass-selected negative ion beam. In a further photodetachment study by Jones *et al*,[6] the cross section for the photodetachment of C_2^- was investigated in the photo energy ranging from 14000 to $20000cm^{-1}$. They observed resonances due to autodetachment at photo energies corresponding to transitions between the high vibrational levels of the X state with ν''=6–10 and the high vibrational levels of the B state with ν'=5–8. Using a merged laser-ion beam spectrometer with sub-Doppler resolution, Mead *et al*[7] studied the B-X

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†E-mail: yqchen@public1.sta.net.cn

transition and obtained the first spectroscopic information of the $A^2\Pi u$ state through its significant perturbations to the B state; thus, they noted that direct observation of the A state would be highly desirable. Based on their results, Rehfuss *et al*[8] observed the A-X transition of C_2^- for the first time. More recently, Royen and Zackrisson[9] studied the band (0,0) of the B-X transition of C_2^- (using velocity modulation spectroscopy), and gave the spin-rotation constant γ' of $\nu'=0$ in the B state by computation simulation fitting to the lineshape because of severely overlapping spectra of two spin components.

In this paper, we use the optical heterodyne magnetic rotation velocity modulation spectroscopy (OH-MR-VMS)[10] to measure the absorption spectra of the hot bands (0,1), (1,2), (2,3) and (3,4) of the C_2^- B-X transition at Doppler-limited resolution in the visible region between 16700 and 17400cm^{-1}. And the band (3,4) is directly measured in absorption for the first time so far as we know. A rotational analysis has been performed and molecular constants have been renewed.

2. Experiment

The experimental apparatus is the same as that for our previous studies for CO^+[11] and N_2^+.[12] Briefly, OH-MR-VMS is a combination of three spectroscopic techniques, i.e., optical heterodyne detection, magnetic rotation and velocity modulation. The frequency modulation (optical heterodyne detection) spectroscopy is used to reduce the amplitude fluctuation greatly from the laser source, the velocity modulation is utilized to suppress the much stronger spectral disturbance of a much more abundant neutral species for ionic selective detections, and the magnetic rotation technique is employed to enhance the signals of paramagnetic molecular ions. All these three techniques are the most favourable to improve the detection sensitivity.[10,13]

The C_2^- negative ions were generated by an ac discharge at 37.7kHz in flowing gases of acetylene and He in a water-cooled absorption cell. The optimum pressure in this paper was critically a mixture of 30Pa of acetylene and 266Pa of He. More than 60 lines of C_2^- in the region 16700–17400cm^{-1} were observed. An additional I_2 reference absorption cell was used to ensure the accuracy of the absolute wavenumber to be better than $\pm$0.007cm^{-1}.

Suppression of spectrum from neutral species by OH-MR-VMS depends on experimental conditions. An improper experimental condition will lead to an observation of spectrum from neutrals. For example, if the waveform of discharge is asymmetric, i.e., the amplitude of one half cycle is bigger than another, it will cause a population modulation at the frequency of velocity modulation, which will give strong spectra of neutral species.

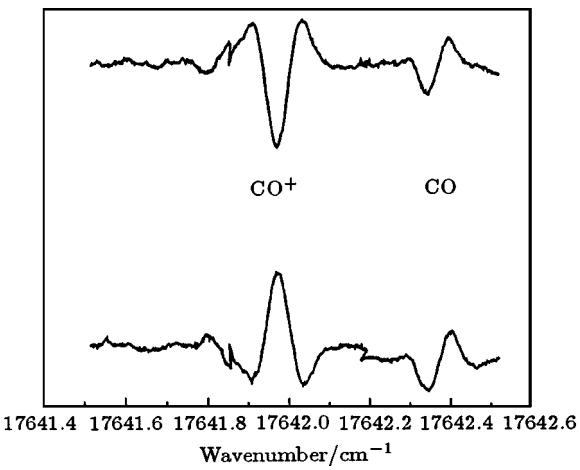


Fig.1. Typical traces of CO^+ and CO spectra. The lineshape of CO^+ is the fourth derivative of Gaussian profile while that of CO is the third derivative due to different modulation mechanism. The upper and lower traces show the results before and after interchanging the discharge electrodes. The spectra phase of CO^+ is reverse while that of CO keeps unchangeable.

Figure 1 shows experimental results when studying CO^+, but for the spectrum of CO^+ comet tail system,[11] the spectrum from CO triplet transitions[14] were also observed in the same region. However, it is easy to discriminate ions from neutrals by their different lineshapes. The spectral lineshape of ions in OH-MR-VMS is the fourth derivative of absorption line in an approximation,[10] while that of neutrals is the third derivative due to the difference of modulation mechanisms. But, if the spectral lines overlap, it is hard to distinguish whether they are from ions or neutrals by the line shapes. For further confirmation, we can interchange the connections of electrodes at the two ends of the discharge cell. The phase of ionic lines will be reversed while that of neutrals will be unchangeable. Because the former depends on the polarity of discharge due to velocity modulation, and the latter depends on the polarity due to population modulation. So, this is a simple way to guide the experiment for optimum experimental conditions to obtain the signals of ions and suppress those of neutrals.

3. Analysis

For the ground X and excited B states, for which Hund's case (b) holds, the rotational Hamiltonian is

$$H = B(r)N^2 - D(r)N^4 + \gamma(r)S \cdot N. \qquad (1)$$

After the transformation, we have the well-known energy expression

$$E = BN(N+1) - DN^2(N+1)^2 + E_{\rm sr}, \qquad (2)$$

where the spin-rotation energies $E_{\rm sr}$ are $\frac{\gamma}{2}N$ and $-\frac{\gamma}{2}(N+1)$ for $F_1\left(J = N + \frac{1}{2}\right)$ and $F_2\left(J = N - \frac{1}{2}\right)$ levels, respectively.

The symmetry of wavefunctions for an individual rovibronic state is specified by the $D_{\infty h}$ molecular symmetry group. Since the ^{12}C nucleus is a boson with I=0, for the ground electronic state with the $X^2\Sigma_g^+$ symmetry, only those levels with even N are allowed.[8]

The energy separation resulting from the spin-rotation splitting is

$$\Delta E = \gamma_\nu(N + 1/2). \qquad (3)$$

The separations of spin components with the same N'' quantum number are determined by the following expressions:

$$\Delta\nu_P(N'') = (\gamma'_\nu - \gamma''_\nu)(N'' + 1/2) - \gamma'_\nu, \qquad (4)$$

and

$$\Delta\nu_R(N'') = (\gamma'_\nu - \gamma''_\nu)(N'' + 1/2) + \gamma'_\nu. \qquad (5)$$

For C_2^-, γ_ν is on the order of 0.005cm^{-1}, which causes two components severely overlap. In our case, the measurement accuracy for the separation of closely located lines is approximately 0.01cm^{-1}. So the values of spin-rotation splitting constants γ_ν could not be meaningfully determined and were neglected.

4. Results and discussion

The observed spectral lines were not abundant due to the transition rule of only even N allowed and the low-J selectivity (typically less than 22)[11] in the magnetic rotational spectroscopy. Altogether over 60 spectral lines in the region 16700–17400cm^{-1} were observed, which belonged to four hot bands (0,1), (1,2), (2,3) and (3,4). We have assigned the observed lines with $R(N)$ and $P(N)$ instead of $R_{11ee}(J)$, $R_{22ff}(J)$, $P_{11ee}(J)$ and $P_{22ff}(J)$ because the branches R_{11ee}/R_{22ff} and P_{11ee}/P_{22ff} with the same N value severely overlap. A part of R branch spectra of the

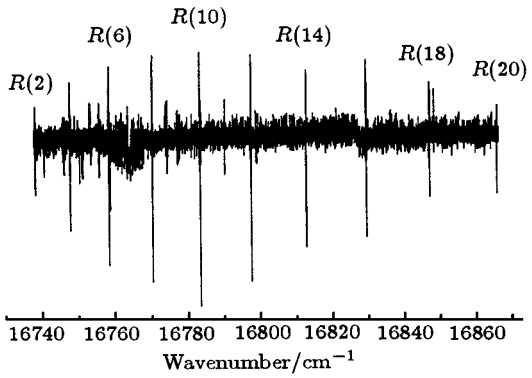


Fig.2. Partial observed rotational spectra of R branch of band (0,1) in the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system of C_2^- by OH-MR-VMS. Due to nuclear spin statistics, only those rotational spectra with even N can be observed.

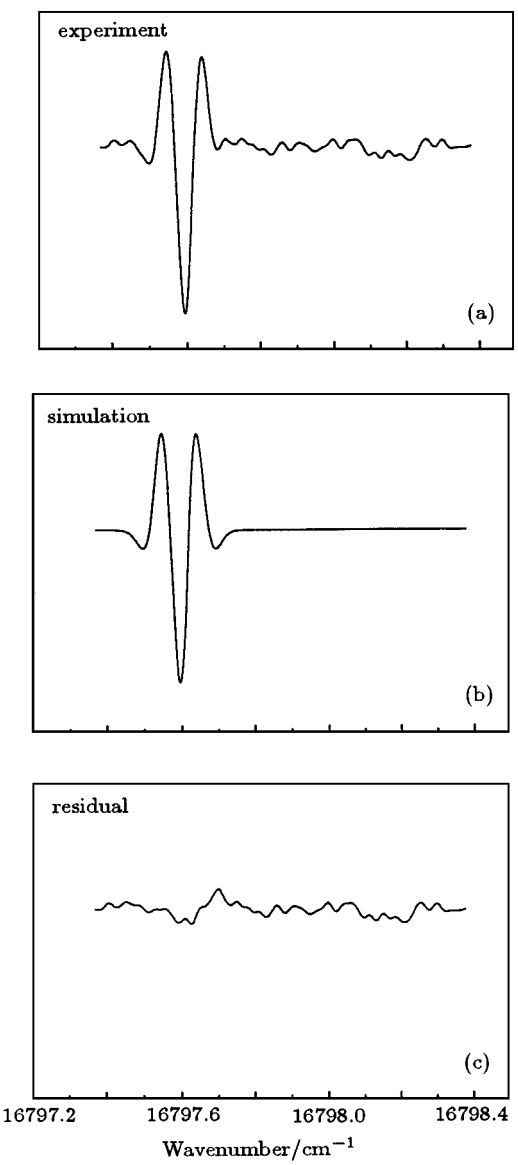


Fig.3. Simulation of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (0,1) band $R(12)$ transition at 16797.595cm^{-1}. (a) the experimental line shape, (b) the theoretical line shape of the fourth derivative of the absorption profile, (c) the residual from the experimental and theoretical lines.

band (0,1) are shown in Fig.2. Normally, the line shapes of frequency modulation[15,16] and velocity modulation spectroscopy[17−19] are the first derivative, and that of Zeeman modulation spectroscopy is the second derivative.[20] The basic line shape of OH-MR-VMS is the fourth derivative of the absorption.[10] In our experiment, the observed line shapes due to ions are all of the fourth derivative of the absorption except for a little asymmetry. A typical line shape and its simulation are shown in Fig.3.

Due to the large rotational constants B_ν and the missing of every alternate line, the spectral lines are widely spaced, with separations about 10cm^{-1}. The accuracy of frequency measurement is on the order of 0.007cm^{-1} in general, except for particularly unfavourable cases where the reference spectral lines are spaced by more than 0.66cm^{-1} or the signal-to-noise ratios are bad. The observed bands (0,1), (1,2) and (2,3) were assigned according to Herzberg and Lagerqvist,[4] and the newly observed band (3,4) was assigned via computing with the extrapolation from their constants. All the lines were bands individually least-squares fitted, and the molecular constants obtained for all vibrational states involved are summarized in Table 1. The standard deviation for the overall least-squares fitting is no more than 0.006cm^{-1}, but that of band (3,4) is 0.01cm^{-1}. Because of the low-J selectivity in the magnetic rotation spectroscopy, the centrifugal distortion constants D_ν in J^4 dependence could not be determined meaningfully. Therefore, the D_ν are fixed at the values obtained by Herzberg and Lagerqvist,[4] while the D_ν of the band (1,2) are floated due to the good signal-to-noise ratios. Because of relatively less observed lines of the band (3,4), the upper state rotational constant B'_3 is also fixed at the value obtained by Herzberg and Lagerqvist[4] in the final fit. The ground state rotational constant B''_4 is directly obtained for the first time. Our results are in good agreement with those in Ref.[4]. Though there are small differences with those of Ref.[6], Jones *et al* obtained these four band constants by a merge analysis instead of individual band fitting. Thus, we consider our results are more reliable.

Table 1. Rotational molecular constants (in cm^{-1}) of $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states of C_2^-.

Molecular	$B^2\Sigma_u^+$		$X^2\Sigma_g^+$	
constant	This work	Ref.[4]	This work	Ref.[4]
B_0	1.86828(10)[a]	1.8685	—	—
B_1	1.849544(65)	1.8499	1.72159(20)	1.72186(23)[c]
B_2	1.83036(11)	1.8308	1.704644(71)	1.7051
B_3	1.8109[b]	1.8109	1.68806(13)	1.6884
B_4	—	—	1.63425(57)	—
$D_0 \times 10^6$	6.88[b]	6.88	—	—
$D_1 \times 10^6$	7.01(20)	7.0	6.69[b]	6.69
$D_2 \times 10^6$	7.1[b]	7.1	6.73(24)	6.6
$D_3 \times 10^6$	7.3[b]	7.3	6.8[b]	6.8

[a]Numbers in parentheses represent the standard errors of last two digits.

[b]Fixed at the values of Ref.[4].

[c]From Ref.[8] because it is more accurate than Ref.[4].

Although four observed bands enabled us to calculate the equilibrium molecular constants, we cannot obtain accurate equilibrium constants due to low vibrational quantum numbers (less than 4). So we use the equilibrium constants obtained by Mead *et al*[7] to construct an RKR potential curve, using the standard computer programs by Le Roy.[21] The obtained RKR curves were used to calculate the Franck–Condon factors[22] for the B-X transition. The calculated Franck–Condon factors are listed in Table 2.

Table 2. The Franck–Condon factors of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system of C_2^-.

	v''				
v'	0	1	2	3	4
0	0.7163	0.2273	0.047	0.008	0.0012
1	0.2503	0.3216	0.2951	0.1025	0.0247
2	0.0318	0.3665	0.1153	0.2777	0.1468
3	0.0017	0.079	0.4002	0.025	0.2227
4	0.00003	0.0056	0.1307	0.3877	0.0003

Therefore, with Franck–Condon principle, the measured relative intensities of all the observed bands, and Boltzmann vibrational distribution in approximation, we estimated the vibrational temperature of C_2^- to be about 3000K. This result differs from 5000K estimated by Refuss *et al.*[8] The possible reason may be the higher pressure of acetylene applied in our experiment. So, the spectral intensities of the four hot bands studied in this paper are less intense than band (0,0) by at least one order of magnitude.

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