

C₆H₂



C₆H₂

строение

18 Б37. Электронное строение триацетилена (в методе линейных комбинаций атомных орбит). Pellegratti Alain. Structure électronique du triacétylène (méthode des combinaisons linéaires des orbitales atomiques améliorée). «C. r. Acad. sci.», 1964, 259, № 14, 2235—2237 (франц.)

1964

С помощью ранее развитого варианта метода МО ЛКАО (РЖХим, 1960, № 20, 79933) рассмотрено электронное строение триацетилена. Для расчета принята модель линейной молекулы (группа симметрии $D\infty h$) с межатомными расстояниями $d_{12}=d_{56}=1,213 \text{ \AA}$, $d_{23}=d_{45}=1,370 \text{ \AA}$, $d_{34}=1,220 \text{ \AA}$. Приведены волновые функции всех занятых и первого свободного уровней (все МО двукратно вырождены). Рассчитанные значения эффективных зарядов равны $q_1=q_6=+0,094$, $q_2=q_5=-0,090$, $q_3=q_4=-0,004$, а порядки π -связей $l_{12}=l_{56}=1,890$, $l_{23}=l_{45}=0,642$, $l_{34}=1,800$. По линейному соотношению $d_{pq}=1,447-0,122 l_{pq}$, вычислены длины связей ($d_{12}=d_{56}=1,216 \text{ \AA}$, $d_{23}=d_{45}=1,369 \text{ \AA}$, $d_{34}=1,227 \text{ \AA}$) в удовлетворительном согласии с их постулированными значениями. Энергии трех первых π -электронных переходов ${}^1\Sigma_q^+ \rightarrow {}^1\Sigma_u^-$, ${}^1\Delta_u$, ${}^1\Sigma_u^+$ равны 5,08, 5,12 и 7,72 эВ. Обсуждается отнесение полос в УФ-спектре. Е. Ш.

2. 1965. 18

1464

H E C=C 3 4
 8 Д105. Электронное строение триацетилена (улучшенный метод линейных комбинаций атомных орбиталей). Pellegratti Alain. Structure électronique du triacétylène (méthode des combinaisons linéaires des orbitales atomiques améliorée). «C. r. Acad. sci.», 1964, 259, № 14, 2235—2237 (франц.)

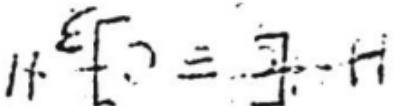
С помощью улучшенного метода МО ЛКАО рассчитаны МО и энергии низших электронных переходов линейной молекулы триацетилена. Использовались слегка теровские АО с эффективным зарядом 3,25. Межатомные расстояния заимствовались из рентгеноструктурных данных. Найдено, что заряды на атомах таковы: $q_1 = q_6 = +0,094$, $q_2 = q_5 = -0,090$ и $q_3 = q_4 = -0,004$; порядки связей равны: $l_{12} = l_{56} = 1,890$, $l_{23} = l_{45} = 0,642$ и $l_{34} = 1,800$.

См. нерб.

9.1965. 88

Применение линейного соотношения длина — порядок связи приводит к межатомным расстояниям, которые почти не отличаются от исходных, что свидетельствует о высокой точности используемого приближения. Вычисленные энергии первых одноэлектронных переходов (в эв) таковы: $\Sigma_g^+ \rightarrow ^1\Sigma_u^-$ 5,08 (запрещен), $\Sigma_g^+ \rightarrow ^1\Delta_u$ 5,12 (запрещен) и $\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ 7,72 (разрешен). Сопоставление полученных результатов с эксперим. данными для углеводородов ряда триацетиlena показывает, что положение максимумов поглощения передается с удовлетворительной точностью.

В. Быховский

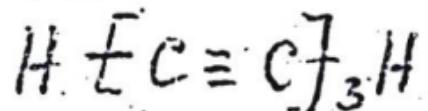


61215.9116

96200

1976

Ph,Ch,TC,MGU



4-15874

Allan Michael, Kloster-Jensen Else, Maier John P. Emission spectra of the radical cations of diacetylene ($\tilde{\Lambda}^2 \Pi_u \rightarrow \tilde{\chi}^2 \Pi_g$), triacetylene ($\tilde{\Lambda}^2 \Pi_g \rightarrow \tilde{\chi}^2 \Pi_u$), and tetraacetylene ($\tilde{\Lambda}^2 \Pi_u \rightarrow \tilde{\chi}^2 \Pi_g, 0^0_0$), and the lifetimes of some vibronic levels of the Λ states.

"Chem. Phys.", 1976, 17, N 1, 11-18

HC:CC:CC:CH On 30925 1988

M.N., Di

110: 659G9g Infrared diode laser spectroscopy of triacetylene by the source and the Stark modulation techniques. Matsumura, Keiji; Kanamori, Hideto; Kawaguchi, Kentarou; Hirota, Eizi; Tanaka, Takehiko (Seinan Gakuin Univ., Fukuoka, Japan 814). *J. Mol. Spectrosc.* 1988, 131(2), 278-87 (Eng). The IR diode laser spectrum of the ν_{11} (π_u : antisym. C:C-H bending) band of triacetylene (HC:CC:CC:CH) was obsd. by the source and the Stark modulation techniques. Precise rotational consts. were derived for the ground and ν_{11} vibrational states. The ν_{11} band origin was 621.33998(23) cm^{-1} with the std. deviation given in parentheses. The Stark modulation spectrum showed a strong feature around the Q-branch head, its lineshape indicating that the ν_8 (π_g : sym. C:C-H bending) state lies above the ν_{11} state. Anal. of the Stark modulation spectrum with the line profile simulation allowed deducing the origin of the IR inactive ν_8 band, $622.38 \pm 0.40 \text{ cm}^{-1}$.

C.A.1989, 110, N8

C_6H_2

1994

121: 45379p Infrared spectra of triacetylene in the 400-220 cm⁻¹ region: absolute band intensity and implications for the atmosphere of Titan. Delpech, C.; Guillemin, J. C.; Paillous, P.; Khelifi, M.; Bruston, P.; Raulin, F. (LISA, 94010 Creteil, Fr.). *Spectrochim. Acta, Part A* 1994, 50A(6), 1095-100 (Eng). The gas phase IR spectra of triacetylene were studied at room temp. in the 4000-220 cm⁻¹ wavenumber region. The abs. intensity of all the bands of noticeable strength were exptl. detd. and the assocd. uncertainties were systematically estd. The data obtained were then used for studying the detectability of C_6H_2 in Titan's atm. by means of IR spectroscopy. The upper limit of mean stratospheric abundance derived from the already available Titan IR spectra (a fraction of ppb) is in agreement with the photochem. model ests.

(U.K.-Czech Rep)

C.A. 1994, 121, NY

C6H2

1994

121: 240777u The high-resolution spectra of the ν_{11} band of triacetylene near 622 cm^{-1} : revised assignments for hot bands. Haas, Sybille; Winnewisser, Gisbert; Yamada, Koichi M. T.; Matsumura, Keiji; Kawaguchi, Kentarou (I. Physikalisches Inst., Univ. Koeln, D-50937 Cologne, Germany). *J. Mol. Spectrosc.* 1994, 167(1), 176-90 (Eng). The rovibrational spectra of triacetylene (C6H2) were recorded for the ν_{11} band in high resoln. by FTIR spectroscopy. The assignments for the hot-band system (ν_{11}, ν_{12}) = (1, 1) \leftarrow (0, 1) have been fully revised, and reliable mol. parameters have been detd. including the rotational and vibrational l-type doubling consts. The assignments have been confirmed by simulation of the absorption profile in the Q-branch region. The intensity perturbation caused by the l-type resonance in the (ν_{11}, ν_{12}) = (1, 1) state has been obsd. and discussed.

Pi, CERMP
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C.A. 1994, 121, N20

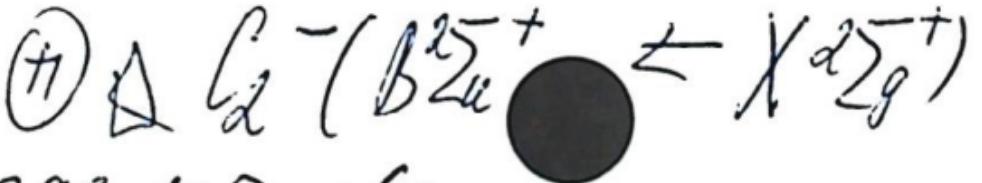
C₆H

C₆H₂⁺

1999

130: 243783q Cavity ring down spectroscopy on radicals in a supersonic slit nozzle discharge. Motylewski, Tomasz; Linnartz, Harold (Institute for Physical Chemistry, University of Basel, CH 4056 Basel, Switz.). *Rev. Sci. Instrum.* 1999, 70(2), 1305–1312 (Eng), American Institute of Physics. A sensitive and generally applicable technique for direct absorption spectroscopy on electronic transitions of transient

species in the gas phase is presented. The method is based on cavity ring down spectroscopy in a pulsed slit nozzle, incorporating a discharge in a high pressure supersonic expansion. The performance is demonstrated with spectra of the 0_o⁰ origin band of the ²Π X²Π electronic transition of the isoelectronic linear C chain radicals C₆H and C₆H₂⁺. Rotationally resolved and rotationally cold spectra ($T_{rot} < 15$ K) were obtained. The sensitivity of the technique is demonstrated for anions with a detection limit $\geq 10^7$ C₂⁻ mols. cm⁻³ for rovibrational transitions of the B²Σ_u⁺ — X²Σ_g⁺ system.



C.A. 1999, 130, N18

$C_6H_2^+$

1999

130: 145573b Rotationally resolved $\text{\AA} ^2\Pi_g - \text{X} ^2\Pi_u$ electronic spectrum of triacetylene cation by frequency modulation absorption spectroscopy. Sinclair, Wayne E.; Pfluger, David; Linnartz, Harold; Maier, John P. (Institute for Physical Chemistry, University of Basel, CH 4056 Basel, Switz.). *J. Chem. Phys.* 1999, 110(1), 296-303 (Eng). American Institute of Physics. The spectrum of the $\text{\AA} ^2\Pi_g - \text{X} ^2\Pi_u$ O_0^0 band system of $C_6H_2^+$ and isotopic derivs. DC_6H^+ and $C_6D_2^+$ were studied at Doppler-limited resoln. using frequency modulation absorption spectroscopy. The ions were generated in a liq.-N-cooled hollow cathode discharge incorporated in a White cell. A discharge modulation in combination with the frequency modulation technique was used to enhance the detection sensitivity. Analyses of the rotational structure yield accurate rotational and spin-orbit interaction consts. of triacetylene cation in the 2 electronic states and information on its geometry.

C.A. 1999, 130, N11