CF_2

1995

23 Б1223. Инфракрасная лазерная спектроскопия полосы ν_2 дифторкарбена (CF_2). Infrared laser spectroscopy of the ν_2 band of difluorocarbene (CF_2) / Qian Hai-bo, Davies Paul B. // J. Mol. Spectrosc. .— 1995 .— **169** , № 1 .— С. 201—210 .— Англ.

В области 638—706 см$^{-1}$ с разрешением, ограниченным допплеровским уширением, измерена (полупроводниковый лазерный спектрометр) вращательная структура полосы ν_2 молекулы $CF_2(\tilde{X}^1A_1)$. Приведено положение и отнесение 217 наблюдаемых линий ($J \leqslant 40$, $K_a \leqslant 7$). При анализе спектра использован A-приведенный гамильтониан Ватсона в I^r-представлении. Значения молекулярных постоянных для основного состояния фиксировали в соответствии с данными исследований микроволновых спектров. Начало полосы при 666,24922 см$^{-1}$. Значения вращательных постоянных A, B и C CF_2 ($\nu_2=1$) (в см$^{-1}$): 2,97347; 0,416141; 0,363055. Приведены также значения параметров центробежного искажения.

В. М. Ковба

М.Л.

Х. 1995, N 23

CF_2 ОМ 38120 1995

Roberto Martinez, Inaki Merelas et al.,

$(\tilde{A}-\tilde{X})$

J. Phys. B: At. Mol. Opt. Phys. 1995, <u>28</u>, 4563–4575.

CF_2 1995

Su, Kehi; Deakyne, C.A., et al.,

(2) Wuli Huaxue Xuebao 1995, 11(10), 865-9

(см. Bet, I)

CF_2 (от 38994) 1997

молекул. стр-ра, колебат. частоты, $\Delta_f H$

Byeong-Keo Cheong+,
Han-Book Cho,

J. Phys. Chem., A 1997, 101, 7901-7906

CF_2 Оп. 39136 1997

Josefredo R. Pliego Jr et al.,

J. Chem. Soc., Faraday Trans.,

Ap, 1997, 93(10), 1881–1883.

ab initio paint

Absolute proton affinity and basicity of the carbenes CH_2, CF_2, CCl_2, $C(OH)_2$, $FCOH$, CPh_2 and fluorenylidene.

CF_2

1997

127: 41511b Determination of A−state stretching frequencies of CF_2 radical. Wang, Chuji; Xiao, Yingsheng; Ran, Qin; Chu, Yiwei; Chen, Congxing; Yu, Shuqin; Ma, Xingxiao (Dep. Chem. Phys., Univ. Sci. Technol. China, Hefei, Peop. Rep. China 230026). *Wuli Huaxue Xuebao* **1997**, 13(4), 297−300 (Ch), Beijing Daxue Chubanshe. Laser induced fluorescence excitation spectroscopy was used to det. the previously ambiguous assignments of A−state stretching frequencies of CF_2 radical under supersonic free jet conditions. The measured frequencies are $\nu'_1 = 1012.1 \pm 0.5 cm^{-1}$, $\nu'_3 = 1180.2 \pm 0.5 cm^{-1}$, which is in good agreement with Cameron's[6] calcn. result. Also, some transitions attributed to the (1,n−2,0)−(0,0,0),n≤6 progressions are 1st reported, and new parameters are derived from the spectra obtained.

ν_i в $\tilde{A}$ сост

C. A. 1997, <u>127</u>, N 3

CF_2

1998

129: 46910g Laser–induced fluorescence studies of jet–cooled CF_2: determination of A–state stretching frequencies. Wang, Chuji; Chen, Congxiang; Dai, Jinghua; Ma, Xingxiao (Department of Chemical Physics, University of Science and Technology of China, Hefei, Peop. Rep. China). *Chem. Phys. Lett.* 1998, 288(2,3,4), 473–480 (Eng), Elsevier Science B.V.. Laser–induced fluorescence (LIF) excitation spectra of the CF_2 $A\ ^1B_1$–$X\ ^1A_1$ system around 250 nm was measured under supersonic free–jet conditions. CF_2 radical was produced by DC–discharge of CF_4 seeded in Ar. Previously ambiguous assignments of the A–state stretching frequencies were exptl. detd. to be $\nu_1'=1012.1$ cm^{-1} and $\nu_3'=1180.2$ cm^{-1}, by analyzing the subband spectra attributed to some of the obsd. progressions (2_0^n, $1_0^1 2_0^{n-2}$ and $2_0^n 3_1^1$ ($n \le 6$)) in which 21 vibronic bands were unambiguously labeled. The measured A–state stretching frequencies do not support King et al.'s assignments [D.S. King, P.K. Schenck, J.C. Stephenson, J. Mol. spectrom. 78(1979) 1], but are in good agreement with Cameron et al.'s theor. assertions [M.R. Cameron, S.H. Kable, G.B. Bacskay, J. Chem. phys., 103(1995) 4475].

лазервозбужд.
флуоресц.

$A\,^1B_1 - X\,^1A_1$

ν_i

C.A. 1998, 129, N4

1999

F: CF2
P: 3

131:134914 Structure and Energetics of Group 14 (IV-A) Halides: A Compara Density Functional-Pseudopotential Study. Escalante, Sigfrido; Vargas, Rubicelia; Vela, Alberto (Departamento de Quimica Inorganica Posgrado Fac de Quimica, Universidad Nacional Autonoma de Mexico, Mexico D.F. 04510, M

? J. Phys. Chem. A, 103(28), 5590-5601 (English) The complete set of MX2 and MX4 (M = C, Si, Ge, Sn, Pb and X = F, Cl, Br, group 14 halides are studied with d. functional theory and quasirelativis effective core potentials. To analyze the role of d. inhomogeneities and asymptotic behavior of the Kohn-Sham effective potential in these mols., following exchange-correlation energy functionals are tested: local, semi (generalized gradient), and hybrid functionals. For comparison, Hartree-

C.A. 1999, 131

results are also presented. Fully optimized geometries are in very good agreement with exptl. available data and with other high-level theor. cal The energy differences assocd. with the dissocn. and disproportionation reactions are reported. Zero-point corrections and at. spin-orbit effects included in these reaction energies. The dissocn. energies predicted at Hartree-Fock level are underestimated, the local energy differences are overestimated, and both the semilocal and hybrid approaches provide the b ests. for these reaction energies. The disproportionation energies, whic commonly used to explore the relative stability of different at. valences a behavior that departs from that commonly known for reactions involving single atom: the local and semilocal disproportionation energies have ver similar values and follow the same trends.

1999

F: CF2
P: 3

130:305739 Measurement of CF3 and CF2 radicals in a hollow cathode CF4 plasma. Fujioka, Hiroyuki; Mashino, Souichi; Aikyo, Satoshi; Goto, Miki; Arai, Toshihiko (Department of Electrical Engineering, Kanagawa Institute Technology, Japan).

Kanagawa Koka Daigaku Kenkyu Hokoku, B, B-23, 69-72 (Japanese) 1999 Neutral CF3 and CF2 radicals in a hollow cathode dc CF4 discharge have been first measured under various discharge currents and CF4 pressures wi quadrupole mass spectrometer, using the threshold ionization technique. has been found that the CF3 and CF2 radical densities were higher than th obtained for other types of discharges.

CF_2 От. 40107 1999

ab initio
геометр.,
колебат.
частоты,
$\Delta_f H$ (расчет)

Martin Schwartz+ and
Paul Marshall+

J. Phys. Chem. A1999,
103, 7900–7906

CF_2^- Om. 40099 1999

Rebecca L. Schwartz, Gustavo E. Davico et al.,

J. Phys. Chem., 1999, <u>A103</u>, 8213-8221.

Singlet-Triplet Splittings in CX_2 ($X=F$, Cl, Br, I)

Dihalocarbenes via Negative Ion Photoelectron Spectroscopy

2000

F: CF2
P: 3
133:302781 Nuclear spin-rotation interaction in CF2 (X 1A1) observed by Fourier transform microwave spectroscopy. Hansen, N.; Mader, H.; Temps, F. Institut fur Physikalische Chemie, Christian-Albrechts-Universitat zu Kiel Kiel D-24098, Germany Chem. Phys. Lett., 327(1,2), 97-103 (English) 2000. The rotational spectrum of difluoromethylene (CF2) in its X 1A1 ground electronic state was obsd. using mol. beam-Fourier transform microwave spectroscopy. CF2 was produced in a free jet expansion in Ar as inert

carrier gas by ArF excimer laser photolysis of CF2Cl2, CF2CHCl, or CF2CHBr or by flash pyrolysis of CF2Br2 in the high-pressure region directly behind a pulsed mol. beam valve. Rotational transitions were obsd. in the frequency range from 8 to 40 GHz in the CF2 (000) ground vibrational state and in the (100), (010), and (001) excited vibrational states. Several obsd. lines were split due to the hyperfine interaction between the 19F nuclear spin and the overall rotation of the mol. The results were used to det. the nuclear spin-rotation interaction parameters for CF2.

F: CF2
P: 3

2000

132:214053 Spectroscopic constants of the X(1A1), a(3B1), and A(1B1) stat of CF2, CCl2, and CBr2 and heats of formation of selected halocarbenes: a initio quantum chemical study.

Sendt, Karina; Bacskay, George B. School of Chemistry, University of Sydney Sydney 2006, Australia J. Chem. Phys., 112(5), 2227-2238 (English) 2000 The geometries, rotational consts., harmonic force consts. and frequencies, dissocn. and term energies of CF2, CCl2, and CBr2 in their r X(1A1), a(3B1) and A(1B1) states, computed by complete active space SCF (CASSCF), complete active space 2nd-order perturbation (CASPT2), and coup cluster with single, double and perturbative triple excitations [CCSD(T)] methods and cc-pVTZ basis sets, are reported. For CCl2 and CBr2 the barr to linearity are characterized. The computed

CA2000, 132

spectroscopic consts. are i good agreement with the available exptl. data. The atomization energies hence heats of formation at 0 and 298 K of these mols. and of CHF, CHCl, CFCl, all in their lowest singlet ground states were computed by the CCSD method using basis sets ranging from cc-pVDZ to aug-cc-pVQZ, cc-pCVQZ and G3large, enabling the extrapolation of the energies to a complete basis s (CBS) limit and the inclusion of core-valence correlation (with the excep of CBr2). Scalar relativistic corrections, computed by CASPT2, were take into account. The final CBS results (in kJ mol-1) are .DELTA.fH2980(CHF) 147 .+-. 4, .DELTA.fH2980(CHCl) = 320 .+-. 4, .DELTA.fH2980(CFCl) = 29 .+ 4, .DELTA.fH2980(CCl2) = 229 .+-. 4, and .DELTA.fH2980(CBr2) = 337 .+-. 8 The GAUSSIAN-3 (G3) heats of formation of these mols. are within 2 kJ mol of the CBS values, representing significant improvement over the GAUSSIAN predictions which differ from the CBS results by up to ~10 kJ mol-1. Similarly, the G3 triplet/singlet energy sepns. are in agreement with tho obtained at the CCSD(T)/cc-pVQZ level of theory including core-valence correlation corrections, as well as expt.