C_2NaH (от. 35591) 1990

9/и 35591.

Botschwina P., Sebald P.

и.п. Chem. Phys. 1990,
141, N2-3, 311-323.

$(HCN)_n$ От 33194 1990

$n = 1, 2, 3$ De Almeida W., Hinchliffe A.;

теор. расчет J. Mol. Struct. Theochem. 1990, <u>204</u>, 153–169.

Mechanical and electrical anharmonicities in the hydro–

gen cyanide hydrogen - bonded clusters.

$(HCN)_{\bar{n}}$ (OM - 35791) ; 33975 1990

Dykstra C.E.,

J. Phys. Chem. 1990, <u>94</u>,
180 - 185.

Intermolecular Vibrational
Frequencies of $(HF)_{\bar{n}}$ and $(HCN)_{\bar{n}}$
Weak Complexes by Electrical

Molecular Mechanics.

$(HCN)_2$ 1990

Gerber R.B., Horn T.R.,
et al.

Dyn. Polyatom. Van der
и.п. Waals Complexes: Proc.
NATO Adv. Res. Workshop,
Castera-Verduzan,
Aug. 21-26, 1989.

New York; London, 1990.
С. 343-354.
(Сер. ХеМе$_2$; $\overline{\underline{III}}$)

HC_3NH^+

1990

ν_3 – полоса, м.п.

114: 14213f **Diode laser spectroscopy of the ν_3 (carbon-nitrogen stretch) band of protonated cyanoacetylene (HC_3NH^+).** Kawaguchi, Kentarou; Kajita, Masatoshi; Tanaka, Keiichi; Hirota, Eizi (Inst. Mol. Sci., Okazaki, Japan 444). *J. Mol. Spectrosc.* 1990, 144(2), 451-3 (Eng). The room temp. diode laser spectra was obsd. for protonated cyanoacetylene with an accuracy of the line positions of 10^{-3} cm^{-1}. The mol. consts. and band origin are given.

C.A. 1991, 114, N2

HC_3NH^+

1990

14 Б1377. Диодная лазерная спектроскопия ν_3(CN валентной) полосы HC_3NH^+. Diode laser spectroscopy of the ν_3 (CN stretch) band of HC_3NH^+ / Kawaguchi K., Kajita M., Tanaka K., Hirota E. // J. Mol. Spectrosc.— 1990.— **144**, № 2.— С. 451—453.— Англ.

На диодном лазерном спектрометре в области частот 2296—2330 см$^{-1}$ с точностью 10^{-3} см$^{-1}$ выполнены измерения колебат. полосы ν_3 (вал. кол. CN) иона HC_3NH^+. Ион генерировался в разряде полого катода в смеси газов HC_3N и H_2. Всего идентифицировано 33 линии ν_3 полосы. Анализ ИК-спектра выполнен с учетом полного вращения линейной молекулы, квартичного и секстичного центробежного искажения. При фиксир. значениях молек. постоянных в основном состоянии определены начало полосы $\nu_3 = 2315{,}1425(4)$ см$^{-1}$, вращат. постоянная в состоянии $\nu_3 = 1$ $B = 4310{,}530(40)$ МГц и постоянная колебательно-вращат. вз-вия $\alpha_3 = 18{,}19$ МГц. Полученные значения спектроскопич. постоянных согласуются с результатами неэмпирич. расчета.

С. Н. Мурзин

М·П·

Х·1991, N 14

$(HCN)_3$ 1990

Kurnig I. J.,
Lischka H., et al.,

J. Chem. Phys. 1990,
структура, 92 (4), 2469–77.
Di, расчет

Linear versus cyclic hydrogen cyanide trimer $(HCN)_3$:

C.A. 1990, 112, N16, 146 011g

an ab initio study on structure, vibrational spectra, and infrared intensities.

$NH_3-(HCN)_2$ 1990

Ruoff R.S.,
Emilsson T. et al.

вращат.
пост.,
структ.

J. Chem. Phys. 1990,
<u>93</u>(9), 6363-70.

(см. $CO-(HCN)_2$; $\underline{III}$)

HN:CHCN
DN:CHCN

1990

Мв спектр,
вр. постоян.

113: 31196z **Microwave spectra, dipole moments, and energy difference of E and Z C-cyanomethanimine (hydrogen cyanide dimer).** Takano, Shuro; Sugie, Masaaki; Sugawara, Koichi; Takeo, Harutoshi; Matsumura, Chi; Masuda, Akimasa; Kuchitsu, Kozo (Natl. Chem. Lab. Ind., Ibaraki, Japan 305). *J. Mol. Spectrosc.* 1990, 141(1), 13–22 (Eng). Microwave spectra of HN:CHCN and DN:CHCN produced by the pyrolysis of Me_2NCN were obsd. and analyzed. The rotational consts. were detd. The energy difference between the *E* and *Z* conformers was detd. as 215(50) cm^{-1} from measurements of the relative intensity and dipole moments for the normal species. The possible mechanism of the pyrolytic reaction for the formation of HN:CHCN from Me_2NCN is discussed.

C.A.1990, 113, N4

CH_3CNH^+ (OM·33940) 1990

Turner B.E., Amano T.,
et al.

Astrophys. J. 1990, 349,
N1, Pt.1, 376-387.

Searches for the protonated
interstellar species HC_3NH^+,

CH_3CN^+ and $HOCS^+$: Implications for ion-molecule chemistry.

HC_3NH^+ От. 33940 1990

Turner B.E., Amano T.
et al.,

Astrophys. J. 1990,
349, N1, Pt 1, 376-
387.

Searches for the protonated interstellar species HC_3NH^+, CH_3CN^+ and $HOCS^+$: Implications for ion-molecule chemistry.

$C_6H_6-N_2$

1990

14 Б1295. **УФ-спектр высокого разрешения вандерваальсовых комплексов бензол—N_2.** Hign-resolution UV spectrum of the benzene—N_2 van der Waals complex / Weber Th., Smith A. M., Riedle E., Neusser H. J., Schlag E. W. // Chem. Phys. Lett.— 1990.— 175, № 1—2. — С. 79—83.— Англ.

Разрешена вращат. структура полосы 6_0^1 электронного перехода $S_1 \leftarrow S_0$ в вандерваальсовом комплексе бензол—N_2 и отнесено 119 переходов. Комплекс $C_6H_6-N_2$ получали в импульсном пучке и детектировали методом масс-селекц. двухфотонной двухцветной спектроскопии с разрешением 100 МГц. Вращат. структура интерпретирована в рамках модели жесткого симм. волчка. Наблюдались слабые дополнит. переходы, возникающие благодаря свободному внутр. вращению N_2 в плоскости, параллельной бензольному кольцу. N_2 располагается параллельно бензольному кольцу на расстоянии 3—5 A от центра, причем это расстояние уменьшается на 45 м A в возбужденном состоянии. Для комплекса определен набор молек. постоянных (в см$^{-1}$):

М·П·

Х. 1991, N 14

$\nu_{00}''=38599{,}307$; $B_0''=0{,}048732$; $C_0''=0{,}0948809$; $B_v'=$
$=0{,}049105$; $C_v'=0{,}090865$. Г. В. Чертихин

рени
еделе
ных

$HNCCN^+$ 1991

115: 145317m Millimeter-wave laboratory detection of ethanedinitrile conjugate monoacid ($HNCCN^+$). Amano, T.; Scappini, Flavio (Herzberg Inst. Astrophys., Natl. Res. Counc., Ottawa, ON Can. K1A 0R6). *J. Chem. Phys.* 1991, 95(4), 2280–2 (Eng). The ground-state rotational spectrum of protonated cyanogen, $NHCCN^+$ was identified following the IR detection by H.E. Warner and T. Amano (1991) using a hollow cathode discharge as prodn. source. The rotational and centrifugal distortion consts. were detd. to be 4438.010 13(71) MHz and 0.529 95(24) kHz, resp.

Вращательн. спектр.

м.п.

C.A. 1991, 115, N14

$NHCCN^+$ C-N-H-[illegible]. 1991

16 Б1145. О возмущении в полосе ν_1 молекулы HNCCN$^+$. On the perturbation observed in the ν_1 band of HNCCN / Botschwina Peter // J. Mol. Spectrosc.— 1991.— **145**, № 2.— С. 454—455.— Англ.

На основании результатов неэмпирич. расчета молекулы NHCCN$^+$ предложена интерпретация локального возмущения полосы ν_1 в районе $I = 25$. В кач-ве наиболее вероятных источников этого возмущения рассмотрены состояния $\nu_3+\nu_4+2\nu_7{}^0$ и $\nu_2+\nu_5{}^1+\nu_6{}^1$; сделан выбор в пользу первого. Отмечен возможный вклад состояния $\nu_3+2\nu_5{}^0$, выражающийся в слабом возмущении большого числа вращат. состояний полосы ν_1.

В. Б. Павлов-Веревкин

М·П-

X·1991, N16

HCCN
CNCN

1991

115: 101775e Ab initio vibration-rotation coupling constants and the equilibrium geometries of ethanedinitrile and cyanogen cyanide (NCCN and CNCN). Botschwina, Peter; Fluegge, Joerg (Inst. Phys. Chem., Univ. Goettingen, W-3400 Goettingen, Fed. Rep. Ger.). *Chem. Phys. Lett.* 1991, 180(6), 589-93 (Eng). The equil. geometries of NCCN and CNCN were calcd. from exptl. ground-state rotational consts. and ab initio values for the vibration-rotation coupling consts. For NCCN, R_{1e}(NC) = 1.1578(5) and R_{2e}(CC) = 1.3839(5) Å were obtained, where estd. error bars are given in parenthesis. The calcd. equil. bond lengths of CNCN are R_{e}(CN) = 1.1813(5), R_{2e}(NC) = 1.3116(5), and R_{3e}(CN) = 1.1581(5) Å. Ground-state rotational and centrifugal distortion consts. are predicted with high accuracy for various isotopomers of NCCN.

расчет
структуры,
м.п.

C.A. 1991, 115, N10

CH_3CN

1991

115: 122735g The rotational spectrum of methyl cyanide-d_3 analysis of the low-lying excited vibrational states. Cosleou, J.; Lopez, J. C.; Alonso, J. L.; Wlodarczak, G.; Demaison, J. (Fac. Cienc., Univ. Valladolid, Valladolid, Spain E-47005). *J. Mol. Spectrosc.* 1991, 149(1), 242-51 (Eng). The rotational spectrum of Me cyanide-d_3 was measured for the vibrational states $v_3 = 1$, $v_4 = 1$, $v_7 = 1$, and $v_8 = 1, 3$. The direct *l*-doubling transitions in the $v_8 = 1$ state were also obsd. The rotational parameters were detd. for these states. A strong Coriolis resonance between the $v_4 = 1$ and $v_7 = 1$ states was obsd. and analyzed. The $v_3 = 1$ state is also perturbed by a Coriolis interaction, but as the other interacting state ($v_6 = 1$) could not be assigned, this interaction was not analyzed.

Вр. спектр.
М.П.

C.A. 1991, 115, N12

$(HCN)_3$

1991

116: 11396y **Mechanical and electrical anharmonicities of the linear hydrogen cyanide hydrogen-bonded trimer.** De Almeida, Wagner B. (Dep. Chem., UMIST, Manchester, UK M60 1QD). *Can. J. Chem.* 1991, 69(12), 2044-52 (Eng). The anharmonicity of the hydrogen-bonded (N...H) and proton donor (C-H) stretching modes of the linear $(HCN)_3$ species are calcd. at the SCF level with the 4-31G and 6-31G** basis sets. Third and fourth energy derivs. and second and third dipole moment derivs., which are needed to calc. the anharmonic terms, were evaluated by means of the one-dimensional Chebyshev polynomial fitting to the calcd. ab initio points. Frequencies and intensities of overtone bands are reported and the effect of geometry relaxation on the polynomial fitted derivs. as well as mech. anharmonicity on the vibrational intensities discussed.

Di, ангармон., теор. расч

C. A. 1992, 116, N2

$CH_2=CH-CH_2-CN$

1991

вращат.-
спектр.,
м.в.

114: 195128a Analysis of the millimeter-wave spectrum of allyl cyanide. Demaison, J.; Burie, J.; Boucher, D.; Wlodarczak, G. (Lab. Spectrosc. Hertzienne, Univ. Lille I, 59655 Villeneuve d'Ascq, Fr.). *J. Mol. Spectrosc.* 1991, 146(2), 455-64 (Eng). The ground state rotational spectra of the cis and gauche forms of allyl cyanide were measured up to 250 GHz. High *J* transitions were assigned for the 2 isomers and accurate centrifugal distortion consts. were detd. The order of magnitude of the centrifugal distortion consts. is discussed. New methods for the anal. of the rotational spectra are proposed. The influence of leverage points is emphasized and a test for their detection is described. The bootstrap and jackknife methods give results in good agreement with the traditional least-square method.

C.A. 1991, <u>114</u>, N 20

1991

NMe_3

Edwards A.H.,

м.п.

J. Chem. Phys. 1991.
$\underline{94}$, N4. с. 2894–2905.

(см. ● NH_3; $\underline{\overline{\mathrm{III}}}$)

$HC \equiv N$

$H_2C = NH$

1991

17 Б1151. Электронные эффекты координации. Строение и колебательные спектры координированных молекул с кратносвязанным донорным атомом / Харабаев И. Н. // Координац. химия.— 1991.— **17**, № 4.— С. 435—442.— Рус.

Неэмпирическим (ОХФ с базисом STO-3G) и полуэмпирич. (MNDO) вариантами метода ССП МО ЛКАО рассчитано строение, силовое поле и колебат. спектры молекул $HC \equiv N$, $H_2C = NH$, $H_2C = O$, $H_2C = S$ и их комплексов с BH_3 и BF_3, на основании чего интерпретированы экспериментально наблюдаемые изменения в колебат. спектрах донорных молекул, происходящие при комплексообразовании. Повышение частоты вал. кол. кратных связей отнесено в случае нитрильных соед. к перегибридизации АО азота, участвующей в образовании σ-составляющей $C \equiv N$-связи, а понижение в случае карбонильных и тиокарбонильных соед. отнесено к нарушению при координации связывающей МО $1\ b_2$ донорной молекулы.

колебат. спектр, структура ☒

+2

Х·1991, №17

HC_9N

1991

115: 37700x Laboratory detection of cyanooctatetrayne (HC_9N) using a Fourier transform microwave spectrometer. Iida, Minoru; Ohshima, Yasuhiro; Endo, Yasuki (Coll. Arts Sci., Univ. Tokyo, Tokyo, Japan 153). *Astrophys. J.* 1991, 371(1, Pt. 2), L45-L46 (Eng). The lab. microwave spectrum of a linear carbon chain mol., HC_9N (cyano-octatetra-yne), was obsd. for the first time by discharging a mixt. of vinylcyanide and acetylene dild. in argon. The absorption spectrum was obsd. in a supersonic beam, using a pulsed-nozzle Fabry-Perot-type Fourier transform microwave spectrometer. Frequencies of 11 rotational transitions were combined with the previously reported astronomical data, yielding accurate ground state parameters, B_0 = 290.518322(57) MHz and D_0 = 0.874(78) Hz.

Вращат. спектр, B_0, D_0

C.A. 1991, 115, N4

$CH_3NH_3^+$ и изотопозамещ. 1991

Сил. пост. среднеквадр. амплитуд колебаний ζe

117: 99762u Molecular dynamics of methylammonium ions and ammonia boranes. Mohan, S.; Settu, K. (Raman Sch. Phys., Pondicherry Univ., Pondicherry, 605 006 India). *Acta Cienc. Indica, Phys.* 1991, 17F(3), 231–42 (Eng). The mol. potential consts. of AX_3XZ_3 type mols., methylammonium ions ($CH_3NH_3^+$, $CH_3ND_3^+$, $CD_3NH_3^+$, and $CD_3NHD_3^+$) and ammonia-boranes (BH_3–NH_3, BD_3–ND_3 and BH_3–ND_3) were evaluated by applying general valence quadratic force fields along with the method of kinetic consts. The other mol. consts. viz., the mean amplitudes of vibration of the bonded and non-bonded at. distances, Coriolis coupling consts. and centrifugal distortion consts. were evaluated.

④ ☒ $BH_3 \cdot NH_3$ и изотопозамещ.

C. A. 1992, 117, N10

$N(CH_3)_3$

1991

11 Д133. Интерпретация колебательного спектра триметиламина с учетом конформационных особенностей / Сербиновская Л. В., Ким С. М., Мулдагалиев Х. Х., Агашкин О. В. // Ж. физ. химии.— 1991.— 65, № 7.— С. 1831—1837.

На основании экспериментальных и рассчитанных колебательных спектров изотопомеров триметиламина (ТМА): $N(CH_3)_3$, $^{15}N(CH_3)_3$, $N(CH_3)_2CD_3$, $N(CH_3)_2CDH_2$, $N(CH_3)(CD)_2$, $N(CD_3)_3$, $^{15}N(CD_3)_3$ проведен отбор фундаментальных частот и сформировано новое силовое поле, учитывающее асимметрию метильных групп. Качество поля проверено по изотопомеру ТМА, который содержит один атом дейтерия и представляет собой равновесную смесь ротамеров. Показано, что расчет с таким силовым полем удовлетворительно описывает колебательные спектры обоих ротамеров.

Резюме

М.Л.

(Н) IX

ф. 1991, N 11

$HNCCN^+$ 1991

114: 32140j **The observation of the ν_1 fundamental and $\nu_1 + \nu_7 - \nu_7$ hot bands of protonated cyanogen ($HNCCN^+$).** Warner, H. E.; Amano, T. (Herzberg Inst. Astrophys., Natl. Res. Council, Ottawa, ON Can. K1A 0R6). *J. Mol. Spectrosc.* **1991**, 145(1), 66–73 (Eng). The ν_1 (N–H stretch) fundamental and $\nu_1 + \nu_7 - \nu_7$ hot band of $HNCCN^+$ were obsd. with the difference-frequency laser system in the hollow cathode discharge. The ion was obsd. in a dry-ice cooled discharge of $(CN)_2$ and H_2, modulated at 10 kHz. The consts. obtained for the fundamental were ν_0 = 3448.2701(1) cm^{-1}, B'' = 4438.22(8) MHz, D'' = 602(25) Hz, B'' = 4430.37(9) MHZ, and D' = 598(26) Hz. For the hot band ν_0 = 3448.2281(1) cm^{-1}, B'' = 4456.22(9) MHz, D'' = 739(61) Hz, B'' = 4448.30(10) MHz, and D' = 741(66) Hz. The values for the fundamental band agree extremely well with the theory.

ν_1, ν_7

вращ. пост.

C.A. 1991, 114, N 4

$HNCCN^+$

1991

14 Б1374. Наблюдение ν_1 основной и $\nu_1+\nu_7-\nu_7$ горячей полос $HNCCN^+$. The observation of the ν_1 fundamental and $\nu_1+\nu_7-\nu_7$ hot bands of $HNCCN^+$ / Warner H. E., Amano T. // J. Mol. Spectrosc.— 1991.— 145, № 1.— С. 66—73.— Англ.

На ИК-лазерном спектрометре, работающем на разностной частоте, в области частот 3432—3463 см$^{-1}$ с точностью около 10^{-3} см$^{-1}$ измерен колебательно-вращат. спектр иона $HNCCN^+$. Ион генерировался в разряде полого катода в смеси газов $(CN)_2$ и H_2. Идентифицировано около 100 линий основной ν_1 полосы и около 150 линий горячей полосы $\nu_1+\nu_7-\nu_7$. Анализ ИК-полос выполнен с учетом полного вращения, квартичного центробежного искажения и колебательно-вращат. вз-вия. Для ν_1 основной и $\nu_1+\nu_7-\nu_7$ горячей полос, соотв., определены начала полос 3448, 2701(1) и 3448,2281(1) см$^{-1}$ и вращат. постоянные $B''=4438{,}22(8)$ и 4456,22(10) МГц, $B'=4430{,}37(9)$ и 4448,30(10) МГц. В спектре наблюдались возмущения, вызванные смешением с соседними колебат. состояниями. С. Н. Мурзин

М.Р.

Х.1991, N14

CH_3CNH^+

1992

(ν_1)

116: 244130x Difference frequency laser spectroscopy of the ν_1 fundamental band of CH_3CNH^+. Amano, T. (Herzberg Inst. Astrophys., Natl. Res. Counc., Ottawa, ON Can. K1A 0R6). *J. Mol. Spectrosc.* 1992, 153(1-2), 654-65 (Eng). The first spectroscopic identification of CH_3CNH^+ was made in a hollow cathode discharge of CH_3CN (~ 10 mtorr) and H_2(~ 500 mtorr) by observing the ν_1 (N-H stretch) fundamental band (ν_0 - 3527.2887 cm^{-1}) with a different frequency laser system. The band was perturbed and some of the *K* structure was not resolved. The spectroscopic consts. were detd. through a least-squares fit of the unperturbed lines. The nature of the perturbation was elucidated in part in an anal. of the perturbed *K* = 1 lines.

C.A. 1992, <u>116</u>, N24

NH_3CH_3

1992

8 Б1038. Теоретический поиск больших ридберговых молекул: NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$ **и** $N(CH_3)_4$. Theoretical search for large Rydberg molecules: NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$, and $N(CH_3)_4$ / Boldyrev Alexander. I., Simons Jack // J. Chem. Phys. — 1992. — **97**, № 9. — С. 6621—6627. — Англ.

На основе неэмпирич. расчетов предсказано существование четырех метастабильных ридберговых молекул: NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$ и $N(CH_3)_4$. Рассмотренные системы имеют локальный минимум на поверхности потенциальной энергии, однако они термодинамически неустойчивы по отношению к отрыву H или CH_3. Определены барьеры диссоциации. Библ. 30. А. А. Сафонов

М. Л. ⊠

Ⓗ

Х. 1993, N 8

● $\left\{ NH_2(CH_3)_2,\ NH(CH_3)_3,\ N(CH_3)_4 \right.$

$NH_3C\dot{H}_3$

$NH_2(CH_3)_2$

$NH(CH_3)_3$

$N(CH_3)_4$

1992

ab initio
расчет

118: 46193y **Theoretical search for large Rydberg molecules: methy derivatives of ammonium radical [NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$, and $N(CH_3)_2$, $NH(CH_3)_3$, and $N(CH_3)_4$].** Boldyrev, Alexander I.; Simons, Jack (Dep. Chem., Univ. Utah, Salt Lake City, UT 84112 USA). *J. Chem. Phys.* 1992, 97(9), 6621-7 (Eng). On the basis of *ab initio* calcns., four new large metastable Rydberg mol.: NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$, and $N(CH_3)_4$ are predicted to exist. All of these neutral species possess high-symmetry local min. but are not thermodynamically stable with respect to loss of H or CH_3. Because they have pronounced barriers on the dissocn. pathways, they should be metastable. The dissocn. barriers for $NH_n(CH_3)_{4-n}$ decompg. to $NH_{n-1}(CH_3)_{4-n}$+H are smaller than for dissocn. into $NH_n(CH_3)_{4-n-1}+CH_3$. Thus, the lifetime of $N(CH_3)_4$ should be much longer than that of NH_4 due to the larger dissocn. barrier and the heavier mass of the departing CH_3 species.

C.A. 1993, <u>118</u>, N6

$HNCC^{15}C^{+}$

1992

②17 Б1177. **Молекулярная структура протонированного дициана, HN/CCN^{+}, по данным спектроскопии в миллиметровой области.** Molecular structure of protonated cyanogen, $HNCCN^{+}$, by millimeter-wave spectroscopy /Cazzoli G., Degli Esposti C., Scappini F. //J. Chem. Phys .—1992 .—97 ,№ 9 .—С. 6187—6190 .—Англ

В области 130—270 ГГц измерены вращат. спектры изотопомеров $HN^{13}CCN^{+}$ (**I**), $HNC^{13}CN^{+}$ (**II**), $H^{15}NCCN^{+}$ (**III**) и $HNCC^{15}C^{+}$ (**IV**) в основном колебат. состоянии. Ранее авторами были исследованы спектры $NHCCN^{+}$ (**V**) и $DNCCN^{+}$ (**VI**). Ионы получали в охлаждаемом от —130 до —150° С разрядном источнике постоянного тока, содержащем смесь $H_2/NCCN/Ar$ (1:1:4). Приведено положение наблюдаемых переходов. Значения вращат. постоянных (в МГц) и постоянных центробежного искажения (в кГц): **I** —4422, 4404, 0,5268; **II** —4417, 16 553, 0,52838; **III** —4320, 49 155, 0,50176; **IV** —4305, 0,2207, 02207, 0,49898; **V** —4438, 01064, 0,53013; **VI** —4158, 32201,

М.П.

X, 1993, N 17

0,45089. Эксперим. значения длин связей R(NH), R(N-C(H)), R(CC), R(CN) в HNCCN$^+$ (в A°):r_0-структура — соотв. 1,0057; 1,140; 1,376; 1,158; r_s-структура 1,005878; 1,14099; 1,37681; 1,15721. Значения длин связей в HNCCN$^+$ сопоставляются с данными по молекулам HCNH$^+$, NCCN, HCN.

В. М. Ковба

епол

$HNCCN^+$

1992

/ 118: 29259g **Molecular structure of protonated cyanogen, $HNCCN^+$, by millimeter-wave spectroscopy.** Cazzoli, G.; Degli Esposti, C.; Scappini, F. (Dip. Chim. "G. Ciamician", Univ. Bologna, I 40126 Bologna, Italy). *J. Chem. Phys.* 1992, 97(9), 6187-97 (Eng). The rotational spectra of the 4 monosubstituted isotopomers of protonated cyanogen $HN^{13}CCN^+$, $HNC^{13}CN^+$, $H^{15}NCCN^+$, and $HNCC^{15}N^+$, in the ground vibrational state were investigated in the spectral region from 130-270 GHz, using a neg. glow discharge prodn. method. From the moments of inertia of the 5 monosubstituted species, including the $DNCCN^+$ isotopomer (C. et al. 1992) and of the parent species $HNCCN^+$ (Amano, T., Scappini, F., 1991), the complete r_s structure was obtained. The alchemy of the ion prodn. was further improved compared to the previous works.

мм спектр,
структурн.
параметры

C.A. 1993, 118, N4

$(HCN)_2$

1992

20 Б1091. Димеры HCN. Фотоэлектронный спектр иминоацетонитрила. HCN dimers: Photoelectron spectrum of iminoacetonitrile /Evans Richard A., Lacombe Sylvie M., Simon Maryse J., Pfister-Guillouzo Geneviève, Wentrup Curt //J. Phys. Chem. .—1992 .—**96** ,№ 12 .—С. 4801—4804 .—Англ.

Исследованы фотоэлектронные спектры одного из изомеров соед. $(HCN)_2$: иминоацетонитрила HN═CH—CN. Детально описана методика его получения пиролизом натриевой соли тозилгидразона цианоформамида при 200° С. По спектрам зафиксировано также небольшое кол-во образующегося мономера HCN. Измеренные вертикальные потенциалы ионизации составили 11,60; 12,34; 13,09; 13,84; 14,51 эВ. С помощью полуэмпирич. квантовохим. расчетов методом МНДП построена схема орбитальных уровней энергии в системе и дана интерпретация эксперим. пиков в спектре. А. В. Немухин

М·Л·

Х. 1992, N20.

$(CH_3NH_3)^+$ 1992

George Biri Lizbeth,
Joe I. Hubert, et al.

(Vi) J. Raman Spectrosc. 1992,
23(7), 417-19.

(см. $P_3O_9^{3-}$; III)

C_6H_5N Оп · 36962 „а" 1992

Hrovat D.A., Waali E.E. et al.,

ab initio расчет J. Am. Chem. Soc. 1992, **114**, 8698 – 8699.

Ab Initio Calculations of the Singlet – Triplet Energy Difference in Phenylnitrene

C_6H_5N

1992

2 Б1180. Фенилнитрен: энергетика, колебательные частоты и молекулярные структуры. Phenylnitrene: Energetics, vibrational frequencies, and molecular structures /Kim Seung-Joon, Hamilton Tracy P., Schaefer Henry F. //J. Amer. Chem. Soc. .—1992 .—**114** ,№ 13 .—С. 5349—5355 .—Англ.

Неэмпирическим методом ССП МО оптимизированы геометрии $^3A_2$ (T_0), $^3B_1$ (T_1), $^3B_2$ (T_2), $^3A_1$ (T_4), $^1A_2$ (S_0), $^1A_1$ (S_1) и $\bar{A}_1$(S_2)-состояний фенилнитрена C_6H_5N (I). Использованы двухэкспонентный (ДЭ) базис и поляризованные базисы ДЭ (*d*) и ДЭ {*d*, *p*). Оптимизация геометрии S_1 проведена также двухконфигурац. методом ССП, T_0, T_1 и S_0 — методом конфигурац. вз-вия с учетом 1- и 2-кратных возбуждений в базисе ДЭ (*d*). Методом ССП в базисах ДЭ и ДЭ (*d*) рассчитаны колебат. частоты и ИК-интенсивности I в указанных состояниях. Вычислены энергии вертикального возбуждения ряда состояний и оценены энергии адиабатич. возбуждения. Основным состоянием

м.п.

Х. 1993, №2

I является T_0; S_0, T_1 и T_2 лежат выше, соотв., на 6200 $см^{-1}$ (17,7 ккал/моль), 18 600 и 32 500 $см^{-1}$. T_0 состояние имеет симметрию C_{2v} и по структуре близко к бензолу, для S_0 характерна заметная альтернация длин связей в цикле, состояние T_1 неплоское. Сопоставление расчетных вращат. постоянных I и цианциклопентадиенильного радикала C_5H_4CN (II) с эксперим. данными свидетельствует в пользу того, что полоса с положением 368 нм в газофазном электронном спектре, приписывавшаяся ^{3}I, в действительности принадлежит II. Библ. 37.

В. Я. Беспалов

$(CH_3)_3CNC$

1992

116: 70999v The millimeter-wave rotational spectrum of tertiary butyl isocyanide. Kisiel, Z. (Inst. Phys., Pol. Acad. Sci., 02-668 Warsaw, Pol.). *J. Mol. Spectrosc.* 1992, 151(2), 396-404 (Eng). The millimeter-wave rotational spectrum of *tert*-butyl isocyanaide, $(CH_3)_3CNC$, was measured in the ground state and in the first excited state of the doubly degenerate CNC bending mode ν_8. Accurate spectroscopic consts. for both states were detd. from frequency measurements spanning the range 146-333 GHz. The results are compared with those for *tert*-Bu cyanide, for which improved ground state sextic distortion consts. are reported. The exptl. quartic centrifugal distortion consts. and the Coriolis coupling const. ζ_8 are well reproduced by a rudimetnary force field calcn. Coriolis coupling consts. for bending modes of linear segments attached to sym. top C_{3v} mols. based on a tetrahedrally substituted carbon atom are compared and factors responsible for changes in their values are identified and discussed.

(мм спектр)

C. A. 1992, <u>116</u>, N8

$N(CH_3)_3$ 1992

$N(CH(CH_3)_2)_3$

Koelmel Ch.,
Ochsenfeld Ch.,
et al.

структурн.
параметры,
V_0

Theor. Chim. Acta
1992, 82 (3-4), 271-
284.

(см. NH_3 ; III)

CH_3NH_4 1992

117: 159780k **The quadrupole coupling tensor of methylamine.** Kreglewski, Marek; Stahl, Wolfgang; Grabow, Jens Uwe; Wlodarczak, Georges (Fac. Chem., Adam Mickiewicz Univ., 60-780 Poznan, Pol.). *Chem. Phys. Lett.* 1992, 196(1-2), 155-8 (Eng). Accurate quadrupole coupling consts. were detd. from the hyperfine splittings of the $J_{K\Gamma}=2_0B_1\leftarrow 1_1B_2$ and $2_1E_1+1\leftarrow 1_1E_1-1$ transitions (Γ being a symmetry label) in the ground state of CH_3NH_2, recorded with a microwave Fourier transform mol. beam spectrometer. These consts., combined with the data for CD_3NH_2 and CD_3ND_2, were used for the calcn. of the diagonal quadrupole coupling tensor.

(Мв Фурье спектр)

C.A. 1992, 117, N 16

$C_2H_6 \cdots HCN$ 1992

Legon A.C., Wallwork A.L. et al.

Вращат. пост. Chem. Phys. Lett. 1992, <u>191</u> (1-2), 97-101.

(см. $C_2H_6 \cdots DCN$; <u>1а</u>)

$CH_3NC \cdots HCCH$ 1992

$CH_3NC \cdots C_2H_2$

Вращат. спектр, структ. параметры, сил. пост.

/ 116: 115951s **Rotational spectrum of isocyanomethane...acetylene and a comparison of the properties of hydrogen bonds NC...HC and CN...HC.** Legon, A. C.; Lister, D. G.; Rego, C. A. (Dep. Chem., Univ. Exeter, Exeter, UK EX4 4QD). *Chem. Phys. Lett.* 1992, 189(3), 221-5 (Eng). Ground-state rotational spectra of 4 isotopomers $CH_3NC...HCCH$, $CH_3NC...HCCD$, $CH_3NC...DCCH$ and $CH_3NC...DCCD$ of a dimer of Me isocyanide and acetylene were obsd. in a pulsed jet. The properties r(C...H–C) and k_σ detd. from the obsd. spectroscopic consts. were compared with the corresponding quantities for the isomer $CH_3CN...HCCH$.

Ⓗ $CH_3NC \cdots C_2H_2$

C.A. 1992, 116, N 12

Акриламид

1992

120: 203150t **Infrared spectrum and normal coordinate calculations of deuterated acrylamide.** Mohan, S.; Sundaraganesan, N. (Raman Sch. Phys., Pondicherry Univ., Pondicherry, 605 014 India). *Arabian J. Sci. Eng.* 1992, 17(4A), 497–504 (Eng). The IR spectrum of deuterated acrylamide as mull was measured in the range 4000–180 cm-1. Normal coordinates treatment of deuterated acrylamide was carried out using general quadratic force field, and the force consts. were refined by the damped least-squares method. The potential energy distributions in both general quadratic space and symmetry coordinates are discussed in relation to the mixing of skeletal frequencies for deuterated acrylamide and the nature of the absorption bands. The vibrational mean amplitudes are also calcd.

ИК спектр, сил. пост.

C.A. 1994, 120, N16

$C_6H_5N^-$ Dn. 36962 1992

Travers M.J., Cowles D.C.,

фотоэл. et al.,
спектр

J. Am. Chem. Soc., 1992,

<u>114</u>, 8699-8701.

Photoelectron Spectroscopy

the Phenylnitrene Anion

CH_5-N_2

1992

118: 261198j Aspects of the CH_5N_2 potential energy surface: diazapropylium ions (CH_3NHNH^+, $CH_3NNH_2^+$ and $CH_2NHNH_2^+$) and diazapropyl radicals (CH_2NHNH_2) studied by theory and experiment. Van Garderen, Harold F.; Ruttink, Paul J. A.; Burgers, Peter C.; McGibbon, Graham A.; Terlouw, Johan K. (Theor. Chem. Group, Univ. Utrecht, 3584 CH Utrecht, Neth.). *Int. J. Mass Spectrom. Ion Processes* 1992, 121(3), 159-82 (Eng). The $CH_5N_2^+$ system has been investigated by ab initio MO calcns. at the CDSD/6-31G**//6-31G** level of theory and by mass spectrometric expts. The calcns. confirm earlier exptl. observations that the diazapropylium ions $CH_3-NH=NH^+$, 1^+, $CH_3-N=NH_2^+$, 2^+ and $CH_2-NH-NH_2^+$, 3^+ and the hydrazonium ion $CH_2=N-NH_3^+$, 4^+, are stable species. Theory predicts 1^+ and 2^+ to be higher in energy than 3^+, by 7-8 kcal mol^{-1}, causing a serious discrepancy with existing exptl values, which indicate that 1^+ and 2^+ are considerably more stable than 3^+. The theor. values are insensitive to inclusion of electron correlation in the geometry detns. From a crit. evaluation of existing energetic data for $N_2H_3^+$, $CH_5N_2^+$ and $C_2H_7N^+$ ions, and collision expts. on deuterium labeled species, it is concluded that theory is correct and that several reported appearance energy (AE) measurements on hydrazines are probably in error owing to interferences from traces of amines. From AE measurements not

потенц. по-верхность

X№1

C.A. 1993, 118, N26

$CH_3-N=NH$

$CH_3-N=N-CH_3$ }(Ap)

affected by these interferences, $\Delta H_f(3^+)$ is proposed to be 204 ± 5 kcal mol^{-1} from which theory leads us to recommend ΔH_f values of 211 ± 5 kcal mol for 1^+ and 2^+. Ab initio calcd. proton affinities for $HN{=}NH$, $CH_3{-}N{=}NH$ and $CH_3{-}N{=}N{-}CH_3$ lead to proposed enthalpies for 1^+ and 2^+ which are consistent with these values. Theory further predicts the ring-closed form of 3^+ to be a remarkably stable species (16.7 kcal mol^{-1} above 3^+) but the hydrogen bridged entity $CH_2{=}N^{H}NH_2^+$ previously proposed to be responsible for the facile interconversion between 3^+ and 4^+, is not a min. on the potential energy surface. In fact, large energy barriers (42-63 kcal mol^{-1}) prohibit interconversion among ions 1^+, 2^+, 3^+ and 4^+, via 1,2-H shifts. Metastable $CH_5N_2^+$ ions dissoc. to HC:N + NH_4^+ and to $HCNH^+$ + NH_3 and in agreement with expt., the reacting configuration for HC:N formation is the ion 4^+. Formation of HC:N from 4^+ is exothermic but the reverse barrier is large (84 kcal mol^{-1}) thus accounting for the persistence of 4^+ in the gas phase and in neutral solvents. The small kinetic energy release (KER) accompanying this reaction is rationalized in terms of ion/dipole attraction in the dissocg. $[HC{:}N{\cdots}NH_4]^+$ complex.

HC_4N

1993

119: 103736z Most stable isomer and singlet–triplet energy separation in the HC_4N molecule. Aoki, K.; Ikuta, S.; Murakami, A. (Computer Center, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji-shi, Tokyo, Japan 192-03). *Chem. Phys. Lett.* **1993**, 209(3), 211-15 (Eng). Geometrical structures of various isomers in the HC_4N mol. were studied by the second-order Moller–Plesset perturbation (MP2) method with the Huzinaga–Dunning D95** basis set. The relative stability was obtained using the single-ref. SDCI+Q method with the general contraction scheme of the [5s3p2d1f(C and N)/3s2p1d(H)] basis set. The most stable isomer is a singlet (1) with a C_3-ring, being 8.6 kcal/mol lower in energy than the triplet linear 6. Several isomers exist within 1 eV of the most stable species.

теор. расчет

C. A. 1993, <u>119</u>, N 10

HC_4N

1993

22 Б1110. Является ли молекула HC_4N в триплетном состоянии линейной. Is a triplet HC_4N molecule linear? /Aoki Kozo, Ikuta Shigeru //J. Chem. Phys. .—1993 .—98 ,№ 9 .—С. 7661—7662 .—Англ.

М.П.

Х.1994, №22

HNCCN+

1993

структура,
ab initio
расчт

118: 93567x **The equilibrium geometry of HNCCN+.** Botschwina, Peter; Fluegge, Joerg; Seeger, Sigrun (Inst. Phys. Chem., Univ. Goettingen, D-W 3400 Goettingen, Germany). *J. Mol. Spectrosc.* 1993, 157(2), 494-8 (Eng). By combining exptl. ground-state rotational consts. and ab initio vibration-rotation coupling consts., an accurate equil. geometry was detd. for $HNCCN^+$: $r_e(NH)$ = 1.0126(5) Å, $R_{1e}(NC)$ = 1.1404(5) Å, $R_{2e}(CC)$ = 1.3731(5) Å, and $R_{3e}(CN)$ = 1.1625(5) Å. Estd. error bars in units of the last digit are given in parentheses. Predictions are made for the rotational, centrifugal distortion, and *l*-type doubling consts. of various isotopomers.

C.A. 1993, <u>118</u>, N 10

$(CH_3)_3CNC$

1993

120: 119664f The rotational spectrum of tertiary butyl isocyanide up to 730 GHz – the observation and classification of the h_3 splitting. Cazzoli, G.; Cotti, G.; Dore, L.; Kisiel, Z. (Dip. Chim. "G. Ciamician", Univ. Bologna, 40126 Bologna, Italy). *J. Mol. Spectrosc.* 1993, 162(2), 467–73 (Eng). The measurements of the rotational spectrum of tert-Bu isocyanide, $(CH_3)_3CNC$, were extended to 730 GHz, J = 124, and K = 90. The new mm-wave and sideband FIR-laser measurements were combined with previous results to yield accurate spectroscopic consts. for the whole frequency region 0–730 GHz. In the highest frequency transitions a splitting in the K = 3 lines was obsd., allowing the detn. of the splitting const. h_3. The known values of h_3 for C_{3v}-type mols. are compared and empirical rules for their behavior are derived and discussed.

(Вращ. спектр)

C. A. 1994, <u>120</u>, N10

$(HCCCN)_2$

1993

119: 213095x Structure and predissociation dynamics of the 2-propynenitrile dimer (($(HCCCN)_2$)): a high resolution infrared study. Kerstel, E. R. T.; Scoles, G.; Yang, X. (Dep. Chem., Princeton Univ., Princeton, NJ 08544 USA). *J. Chem. Phys.* **1993**, 99(2), 876-84 (Eng). The IR spectrum of the HCCCN dimer has been studied using the optothermal technique. Both the ν_1 and ν_2 fundamentals have been recorded. Several hot bands pertaining to these two bands were also obsd. The ν_1 band and the $\nu_1 + \nu_{17} - \nu_{17}$ hot band have been analyzed to yield accurate mol. consts. for both the upper and the lower states. The structure of the HCCCN dimer is detd. to be linear. The red shift of the ν_1 dimer band (outside C-H stretch) from the corresponding monomer band is 2.95 cm^{-1}, while the red shift of the inside C-H stretching fundamental band ν_2 is about 67 cm^{-1}. The predissocn. lifetime of the $\nu_1 = 1$ state is in the range from 90 μs to 16 ns, while the predissocn. lifetime of the $\nu_2 = 1$ state is about 450 ps. All obsd. hot bands which involve the ν_2 vibration show narrower line widths than the fundamental ν_2 band. An explanation of this phenomenon is offered which involves the angular dependence of the dynamic coupling between the inside C–H stretching and the predissocn. coordinate.

ИК-спектр

C. A. 1993, 119, N 20

Триметиламин

1993

118: 48175t Vibrational spectrum and harmonic force field of trimethylamine. Murphy, W. F.; Zerbetto, F.; Duncan, J. L.; McKean, D. C. (Steacie Inst. Mol. Sci., Natl. Res. Counc. Canada, Ottawa, ON Can. K1A 0R6). *J. Phys. Chem.* 1993, 97(3), 581 (Eng). IR and Raman spectra are reported for the isotopic species trimethylamine-d_0, -d_3, -d_6, -d_8, and -d_9. Revised assignments are presented for several bands, in particular in the Me deformation region. Ests. of the harmonic vibrational frequencies were made with an empirical procedure based on Dennison's rule. The mol. structure and harmonic force field were calcd. at the ab initio MP2/6-31G* level of theory, and the force field was fit to the harmonized exptl. frequencies by use of eight independent scale factors. The quality of the fit is excellent (std. deviation: 2.4 cm^{-1}), and the results are notable in that the largest variation between the various scale factors is about 1%. The latter result implies that, for this mol., the vibrational coordinates are accurately described by the unscaled ab initio calcn.

(ИК, СКР, анг. пост.)

С.А. 1993, 118, N6

$(HCN)_{2\div4}$ 1993

Panas I.,

структура, теор. расчет.

Chem. Phys. Lett., 1993, 216, (1-2), 173-9.

(См. $(HF)_{2\div4}$; III)

HC_5N

1993

119: 169476w Vibrational frequencies from microwave data: semirigid bender prediction of the ν_{11} bending fundamental of pentadiynenitrile. Ross, Stephen C. (Dep. Phys., Univ. New Brunswick, Fredericton, NB Can. E3B 5A3). *J. Mol. Spectrosc.* 1993, 161(1), 102-8 (Eng). A suitably extended version of the semirigid bender Hamiltonian of Bunker and Landsberg (J. Mol. Spectrosc. 34, 59-75 (1983)) is applied to the available microwave data for HC_5N, including satellite transitions involving the low frequency ν_{11} bending vibration. The resulting nonlinear least-squares fitting of the semirigid bender Hamiltonian allows a prediction for the ν_{11} vibrational energy. The result of fitting two models for this vibration is that the $\nu_{11}{}^{1}{:}l^{1} \leftarrow 0^0$ transition is predicted to lie at approx. 102 cm^{-1}. This is significantly higher than previous predictions of about 75 cm^{-1}. Experience with other mols. suggests that the current prediction should be within about 10% of the actual vibrational frequency.

$(\nu_i, 4\delta)$

C. A. 1993, 119, N 16

$(CH_3)_2C_5H_3N$ 1993

вращат-
спектр

120: 147460c The microwave spectrum of 2,6-lutidine, analysis of internal rotation and ^{14}N hyperfine structure. Thomsen, C.; Dreizler, H. (Inst. Phys. Chem., Christian-Albrechts-Univ. Kiel, 24098 Kiel, Germany). *Z. Naturforsch., A: Phys. Sci.* 1993, 48(11), 1093-101 (Eng). The rotational spectrum of 2,6-lutidine, $Me_2C_5H_3N$, was recorded between 6 and 26.5 GHz using pulsed mol. beam microwave Fourier transform spectroscopy. The rotational consts. are A = 3509.7139(84) MHz, B = 1906.8639(101) MHz, and C = 1254.6215(14) MHz, the barrier to internal rotation of the 2 Me groups is V_3 = 1.1752 kJ/mol, their moments of inertia are I_α = 3.0805(9) uÅ². The N nuclear quadrupole consts. are χ_{aa} = +1.600(5) MHz, χ_{bb} = −4.572(3) MHz and χ_{cc} = +2.972(5) MHz.

C.A. 1994, 120, N12

HCCCN – HCN

1993

ν_1, ИК спектр высокого разрешение

119: 82363h **A high-resolution infrared study of 2-propynenitrile–hydrogen cyanide and 2-propynenitrile–hydrogen fluoride (HCCCN–HCN and HCCCN–HF).** Yang, X.; Kerstel, E. R. T.; Scoles, G. (Dep. Chem., Princeton Univ., Princeton, NJ 08544 USA). *J. Chem. Phys.* **1993**, 99(1), 760–1 (Eng). In a high-resoln. IR study of the H-bonded complexes HCCCN–HCN and HCCCN–HF the results for the ν_1 band of HCCCN–HCN and the ν_2 band of HCCCN–HF are analyzed and compared with the C–H stretch bands obtained previously for HCN–HCN, HCCCN–HCCCN and HCN–HF. The ν_1 fundamental band involves the outside C–H stretching vibration assocd. with the HCCCN unit. The ν_2 band is due to a C–H stretch involved in the H bond.

(H) ☒ HCCCN – HF (ν_2, ИК спектр выс. разрешен.)

C. A. 1993, 119, N 8

$C_3H_6{}^{14}NH_3$

1994

Мв спектр, вращат. пост., r_e

120: 203190f **The microwave spectrum of cyclopropane·ammonia. A novel structure for cyclopropane complexes.** Forest, Susan E.; Kuczkowski, Robert L. (Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055 USA). *Chem. Phys. Lett.* 1994, 218(4), 349-52 (Eng). The microwave spectrum of the cyclopropane-ammonia ($C_3H_6\cdot{}^{14}NH_3$) complex has been obsd. using a pulsed nozzle, Fourier transform microwave spectrometer. The spectrum is characteristic of a sym. top, B_0 = 2668.7161(4), with free internal rotation of the NH_3 subunit. The spectra of the $C_3H_6\cdot{}^{15}NH_3$, $C_3D_6\cdot{}^{15}NH_3$, and $C_3H_6\cdot{}^{14}ND_3$ isotopomers were also measured. This gives a structure in which the nitrogen of the ammonia interacts with the top of the cyclopropane ring, resulting in a stacked structure with R_{cm} = 3.657(3). The quadrupole coupling const. of the nitrogen nucleus is eQq = −2.509(2) MHz.

C.A. 1994, 120, N16

HC_5N

1994

122: 91800n The high-resolution infrared spectrum of cyanobutadiyne, HC_5N: the ν_7 band centered at 642 cm^{-1}. Haas, Sybille; Winnewisser, Gisbert; Yamada, Koichi M. T. (I. Phys. Inst., Univ. Koeln, D-50937 Koeln, Germany). *Can. J. Phys.* 1994, 72(11&12), 1165–78 (Eng). The ν_7 IR band of cyanobutadiyne (HC_5N) was recorded for the 1st time with high resoln. by FTIR spectroscopy using a sample produced by gas elec. discharge. The fundamental and the hot bands arising from the ν_{11} = 1 and 2 states are identified. The mol. parameters, including the rotational and vibrational l-type doubling consts., were detd. accurately by analyzing the spectra together with the available microwave and millimeter wave data. The intensity perturbation caused by the l-type resonance in the (ν_7,ν_{11}) = (1,1) state was clearly obsd. and discussed.

(ν_7)

C.A. 1995, 122, N8

Диметилацетамид

1994

123: 43302a Vibrational spectra and normal coordinate analysis of N,N-dimethylacetamide. Mohan, S.; Murugan, R. (Raman School of Physics, Pondicherry University, Pondicherry, 605 014 India). *Proc. Natl. Acad. Sci., India, Sect. A* 1994, 64(3), 391–9 (Eng). Raman and FTIR spectra of N, N-dimethylacetamide were recorded. The vibrational frequencies were assigned to various modes of vibration from normal coordinate calcn. using simplified general valence force field. Potential energy distribution of the various modes of vibration study the nature of the absorption frequencies and to make unambiguous vibrational assignment. A least square technique was used to refine the force consts.

(СКР, сил. пост., Di)

С.А. 1995, 123, N4

HC_4CN

1994

вращат. постоян., ab initio

122: 170652u **Ab initio rotational constants of the nitriles derived from cyanodiacetylene (HC_4CN).** Moreno, Raul; Silla, Estanislao; Tunon, Inaki; Arnau, Arturo (Departmento de Quimica Fisica, Universidad de Valencia, Burjassot, Spain 46100). *Astrophys. J.* 1994, 437(1, Pt. 1), 532–9 (Eng). The rotational consts. and the dipole moments of the 14 hydrogenated nitriles derived from cyanodiacetylene, its isomers, and those conformers for which exptl. data is available have been calcd. with ab initio methods. The high dipole moment of these compds., the presence of cyanodiacetylene in different regions of space, as well as the great abundance of hydrogen in the dense clouds could lead to the detection of the species being studied here in the interstellar medium.

C. A. 1995, 122, N 14

$H_2C-H^+ \cdots NH_3$

1994

121: 92417j An Investigation of the Acidic Properties of the Methyl Cation and Its Possible Role as a Hydrogen Bond Donor. Characterization of Complexes of the Type [$H_2C-H^+ \bullet\bullet\bullet B$] (B = NH_3, H_2O, and HF). Uggerud, Einar (Department of Chemistry, University of Oslo, N-0315 Oslo, Norway). *J. Am. Chem. Soc.* **1994,** 116(15), 6873-9 (Eng). Results of quantum chem. calcns. of the title complexes show that they are strongly bonded. The bond dissocn. enthalpies (298 K) of the $H_2C-H^+\cdots B$ bonds were calcd. to be 85-88, 71-74 and 44-47 kJ mol^{-1} for B = NH_3, H_2O, and HF, resp. The periodic trend in the bond dissocn. enthalpies, C-H vibrational frequencies, and C-H bond lengths is found to be in accord with a model of the interaction which in addn. to the normal ion/dipole terms incorporates a variable amt. of hydrogen bonding. The hydrogen bond character is most pronounced in the complex with ammonia and practically absent in the complex with hydrogen fluoride. The complex with water represents an intermediate situation. The role of this general type of complexes in gas-phase and condensed-phase reactions is discussed.

($Д_{298}$)

(+2) ☒I

1) $H_2C-H^+ \cdots H_2O$

2) $H_2C-H^+ \cdots HF$

С.А. 1994, <u>121</u>, N8.

C-N-H соед.

1995

Триазин

123: 211697d **FTIR investigation of the IR-inactive fundamental ν_{14} of 1,3,5-triazine via combined analysis of the hot band $\nu_{12} + \delta_{14}-\nu_{14}$ and the combination band $\nu_{12} + \nu_{14}$.** Bodenmueller, Wolfram; Ruoff, Andreas (Sekt. Schwingungsspektrosk., Univ. Ulm, D-89069 Ulm, Germany). *J. Mol. Spectrosc.* 1995, 173(1), 205–22 (Eng). The vibration-rotation spectra of the $\nu_{12}(A''_2)$, $\nu_{12} + \nu_{14}-\nu_{14}(E' \otimes E'')$ bands for 1,3,5-triazine have been measured with an FTIR spectrometer, with the spectra resoln. being about 0.002 cm^{-1}. A set of accurate mol. consts. has been detd. for the ground state, and the excited states $v_{12} = 1$ and $v_{12} = \nu_{14}-\nu_{14}$ band is found t have pronounced PAPE structure. From a suitable combination of lines of $\nu_{12} + \nu_{14}$ and $\nu_{12} + \nu_{14}-\nu_{14}$, more than 1400 transitions of the IR-inactive $\nu_{14}(E'')$ have been obtained. The mol. consts. of the state $v_{14} = 1$ have been detd., with the std. deviation being about 2.6×10^{-4} cm^{-1}.

(Vi)

C.A. 1995, 123, №16

1995

F: CHN2-

P: 3

11Б1109. CHN[2]{-}. Анион-бирадикал и новый тип реакционноспособного интермедиата. CHN[2]{-}: A biradical anion and a potentially new type of reactive intermediate / Gordon M. S., Kass S. R. // J. Phys. Chem. 1995. - 99, N 17. - С. 6548-6550. - Англ. Место хранения ГПТБ еэмпирическим методом МК ССП в базисе 6-31 ++ ГФ{*}{*} выполнены расчеты изомеров аниона диазиринила (I) и его изомера симметрии C[2v] (II), в к-ром два атома азота не связаны друг с другом. Показано, что изомер II представляет собой бирадикал-анион и является реакционноспособным интермедиатом нового типа; изомер характеризуется высоким значением энергий связи электрона ('ЭКВИВ'0,8 эВ). Теплоты образования диазометана и диазирина рассчитаны в приближении теории Гауссиан-2.

X. 1996, N 11

(HCN)n

1995

123: 96305k Structure and spectroscopy of (HCN)$_n$ clusters: cooperative and electronic delocalization effects in C–H•••N hydrogen bonding. King, Bretta F.; Weinhold, Frank (Theoretical Chem. Inst. Dep. Chem., Univ. Wisconsin, Madison, WI 53706 USA). *J. Chem. Phys.* **1995**, 103(1), 333–47 (Eng). We investigate ab initio energetic, structural, dielec., and IR spectroscopic properties of linear (HCN)$_n$ clusters (extending the theor. levels and cluster sizes previously considered) to quant. characterize cooperative effects in C–H···N hydrogen bonding that may be amenable to exptl. detection. Our results indicate that large cooperative effects should be evident in H–bond energies (~90% increase), intermol. sepns. (~0.10–0.15 Å shrinkage), av. dipole moments (~25% increase), and, particularly, in CH stretching frequencies (~100 cm^{-1} shift) and intensities (~300%–400% increase per monomer) as cluster size increases. Such non-pairwise-additive effects lie outside the scope of empirical potentials in common usage, and thus reflect fundamental inadequacies of these potentials and the underlying "electrostatic" picture of H bonding. We employ natural bond orbital (NBO) anal. to examine the detailed electronic origins of cooperative effects, particularly the dramatic ir intensity enhancements that may provide a unique spectroscopic signature of concerted intermol. charge shifts. nBO anal. suggests how the nonlinear cooperativity effects can be rationalized in terms of the fundamental $n_N \rightarrow \sigma_{CH}^*$ "charge transfer" ("resonance") nature of H bonding, manifested even in low-polarity H bonds involving CH groups.

теор. расчет
ИК спектр

CA 1995, 123 N8

$NH_3 ... HC_4H$ 1995

123: 240539j **Calculated spectroscopic properties for $NH_3...HC_4H$.** Schulz, Bernd; Botschwina, Peter (Institut fuer Physikalische Chemie, Universitaet Goettingen, Tammannstrasse 6, D-37077 Gottingen, Germany). *Chem. Phys. Lett.* **1995,** 243(5,6), 378-86 (Eng). The hydrogen-bonded hetero-dimer $NH_3...HC_4H$ has been investigated by means of the CEPA, making use of a basis set of 210 contracted Gaussian-type orbitals. The equil. dissocn. energy is estd. to be 17.5±1.0 kJ mol^{-1} and the equil. dipole moment is $\mu_e = -2.468$ D, with the pos. end at the site of the ammonia protons. Compared to the IR-active antisym. CH stretching vibration of free diacetylene the wavenumbers of the CH vibrations in the complex are reduced by 126.6 cm^{-1} (inner CH stretch) and increased by 4.7 cm^{-1}. (outer CH stretch). The corresponding intensity ratio is 5.8. The pseudosym. acetylenic CC vibration has a large intensity of 20 km mol^{-1}. The intensity of the sym. NH stretching vibration is smaller than in free NH_3 by a factor of 2.

(D_0, ν_i)

C. A. 1995, 123, N18

Цианоген,
изоцианоген и др.

1995

125: 43862z Theoretical study of the electronic spectra of some linear chain tetraatomic molecules. Singh, Chandrama; Singh, S. Nath (DEPARTMENT PHYSICS, MAGADH UNIVERSITY, Bodh, 824234 India). *Acta Cienc. Indica, Phys.* **1995**, 21(1), 1–8 (Eng). The valence and Rydberg electronic states of some linear chain tetra–atomics like cyanogen, isocyanogen, isocyanic acid, and para–cyanic acid calcd. under semi–empirical SCF–MO–MR INDO/S scheme, are presented. The ionization potentials, S–S, S–T transitions and S–T splittings for these mols. are discussed. The paper is provided with exptl. correlations as well.

теор. исслед.
электр. спектр.

C. A. 1996, 125, N4

$((CH_3)_2NH)_2$ 1995

Wales D.J., Stone A.J.
et al.
Chem. Phys. Lett.
1995, 240 (1,2,3), 89-96.

потенц.
поверхн.,
теор.
расчёт

(см. $Ar \cdot NH_3$; III)

Цианоацетилен 1995

124: 245193x **Sub-millimeter wave spectra of cyanoacetylene and revised ground state constants.** Yamada, K. M. T.; Moravec, A.; Winnewisser, G. (I. Physikalisches Inst., Univ. zu Koeln, D-50937 Cologne, Germany). *Z. Naturforsch., A: Phys. Sci.* **1995**, 50(12), 1179-81 (Eng). Sixteen new rotational transitions of cyanoacetylene in the ground vibrational state were measured at 570-710 GHz by the Cologne sub-mm-wave spectrometer. The obsd. transition frequencies were analyzed together with unpublished mm-wave data of the authors group and with the data available in the literature. Precise rotational const. and the quartic and sextic centrifugal distortion consts. were detd.; $B = 4549.058224(37)$ MHz, $D = 0.544110(19)$ kHz, and $H = 0.0345(21)$ mHz.

(мм спектр)

C.A. 1996, 124, N18

$(HCCCN)_n$ 38156 1995

$n>3$

124: 17668a High resolution infrared molecular beam spectroscopy of cyanoacetylene clusters. Yang, X.; Kerstel, E. R. Th.; Scoles, G.; Bemish, R. J.; Miller, R. E. (Dep. Chem., Princeton Univ., Princeton, NJ 08544 USA). *J. Chem. Phys.* **1995**, 103(20), 8828–39 (Eng). High resoln. IR optothermal spectroscopy has been used to study small clusters of cyanoacetylene, $(HCCCN)_n$, contg. three or more monomer units. For the linear HCCCN trimer the fundamental of the free C–H stretch vibration has been rotationally resolved and analyzed, yielding a ground vibrational state rotational const. (B_0) of 94.031(13) MHz. In addn., an inner C–H stretch fundamental band of the linear trimer (rotationally unresolved) has been identified by observing the effect of large elec. fields on the band shape. This assignment is also consistent with spectral intensity measurements as a function of mol. beam stagnation pressure. Predissocn. lifetimes of the upper states of these two bands were detd. from the obsd. homogeneous linewidths. Several other rotationally unresolved vibrational bands have also been obsd. The stagnation pressure and elec. field dependence of these spectra are used to est. the cluster sizes and to make tentative structural assignments.

(ИК, ν_i)

C.A. 1996, <u>124</u>, N2

$(HCCCN)_{n}$ Om. 38156 1995

Yang X., Kerstel E.R.Th., Scoles G., et al.,

(UK)

J. Chem. Phys., 1995, <u>103</u> (20), 8828–

HC_5N 1996

Botschwina, Peter;

Chem. Phys. Lett. 1996,
<u>259</u> (5, 6), 627–634

(D_0,
C–H)

(См. C_5N; $\overline{\underline{III}}$)

1996

$(HCN)_n$

$(HC_3N)_n$

структура,
стабильн.,
теор. расчет

125: 68256t Linear and Cyclic Clusters of Hydrogen Cyanide and Cyanoacetylene: A Comparative ab Initio and Density Functional Study on Cooperative Hydrogen Bonding. Karpfen, Alfred (Institut fuer Theoretische Chemie und Strahlenchemie, Universitaet Wien, A−1090 Vienna, Austria). *J. Phys. Chem.* **1996**, 100(32), 13474–13486 (Eng). The equil. structures, the stabilization energies, the harmonic vibrational spectra, and the IR intensities of linear and cyclic hydrogen cyanide, $(HCN)_n$, and cyanoacetylene oligomers, $(HC_3N)_n$, were calcd. at the ab initio SCF and at the Moller−Plesset second−order level, as well as with the aid of a d. functional method. Several extended basis sets were applied. The systematic modifications of the most important properties characteristic for the C−H− − −N hydrogen bond in these two series of intermol. clusters, in particular, the intermol. distances, R(H− −N), the intramol. distances, R(C−H), the interaction energies per hydrogen bond, with and without zero−point energy corrections, the C−H stretching frequencies, n(C−H), and their corresponding IR intensities were monitored as a function of the oligomer size and are discussed in detail. The mode of convergence to the infinite chain limit is described and found to be qual. quite similar in both systems. From a quant. point of view, all features usually attributed to hydrogen−bond nonadditivity are somewhat weaker for the cyanoacetylene clusters;this is mainly a consequence of the mol. size. Tentative assignments are suggested for the IR active vibrations of larger cyclic cyanoacetylene clusters.

C.A.1996, 125, N6

HC_5-N^+. 1996

Lee, Sungyul,

структура, Di, ν, теор. расчет.

J. Phys. Chem., 1996
<u>100</u> (33), 13959-13962

1996

F: C-H-N
P: 3
9Б1194. Электронографическое исследование структуры, внутреннего вращения и колебательные спектры N,N-диэтилцианамида / Кучкаев Б. И., Князев Б. А., Васильев А. С. // Ж. структур. химии. - 1996. - 37, N 3. - С. 479-486. - Рус.

Получены молекулярные характеристики - структурные параметры, параметры внутреннего вращения, частоты нормальных колебаний N,N-диэтилцианамида. Геометрическое строение и внутреннее

РЖХ 1997

вращение исследовано методом газовой электронографии. Найдено, что конфигурация связей аминного атома азота близка к пирамидальной: <'=='CNC 111,8°; <CNC 109,1°; основные длины связей (A): N'=='C 1,174; '=='C-N 1,349; C-N 1,479; C-C 1,536. Построена карта изменения конформационных энергий при вращении этильных групп вокруг связей N-C. Получены экспериментальные ИК- и КР-спектры чистой жидкости и р-ра в CCl[4]. Проведен расчет частот и форм нормальных колебаний и определены силовые постоянные.

$NH_3-H-C⋮C-CH_3$ 1996

126: 162533y **Ab initio calculations for propyne and the hydrogen-bonded complex NH_3-H-C⋮C-CH_3.** Schulz, Bernd; Botschwina, Peter (Inst. Phys. Chem., Univ. Goettingen, D-37707 Goettingen, Germany). *Mol. Phys.* **1996**, 89(5), 1553-1565 (Eng), Taylor & Francis. The hydrogen-bonded cluster NH_3-H-C⋮C-CH_3 has been investigated by means of the CEPA, making use of a basis set of 198 contracted Gaussian-type orbitals. The calcd. equil. structure is r_{1e}(N-H) = 1.0127 Å, α_e (∠ HN-H) = 112.32°, R_{1e}(N-H) = 2.3593 Å, r_{2e}(acetylenic C-H) = 1.0690 Å, R_{2e}(C⋮C) = 1.2078 Å, R_{3e} (C-C) = 1.4711 Å, r_{3e}(C-H) = 1.0894 Å and β_e(∠ CCH) = 110.50°. The recommended equil. dissocn. energy is $D_e = 12.4 \pm 0.5$ kJ mol^{-1} and the calcd. equil. dipole moment is μ_e = -1.468 D, with the pos. end of the dipole at the ammonia protons. Harmonic wave nos. and abs. IR intensities for the totally sym. modes are calcd. Compared with free propyne the acetylenic CH stretching vibration experiences a bathochromic shift of 93 cm^{-1} and an intensity enhancement by a factor of 5.5.

(ab initio
расчет
м.п.)

C.A. 1997, 126, N 12

Диметиламин

C-N-H

1996

124: 299408q Symmetry properties of inversion–bending Hamiltonian of dimethylamine. Senent, M. L. (Dep. Chem., Brock Univ., St. Catharines, ON Can. L2S 3A1). *Int. J. Quantum Chem.* **1996,** 58(4), 399–406 (Eng). The coupling between the NH hydrogen inversion and the CNC bending modes of dimethylamine (DMA) is analyzed from ab-initio calcns. For this purpose, the vibrational Hamiltonian is defined from the symmetry properties of the kinetic and potential operators. The two fundamental frequencies are detd. with the Moeller–Plesset perturbation theory up to four order (MP4). Calcd. band positions are compared with data derived from other models in one dimension that reveal the strong effect of the interaction terms on the inversion bands. The frequencies of two components of the wagging fundamental are obtained to be 794.3 and 793.4 cm^{-1} with the two-dimensional model, in good agreement with exptl. data.

(Di)

C. A. 1996, 124, N 22

H_2 CCN

1996

124: 130228v Time-resolved infrared diode laser spectroscopy of the ν_5 band of the cyanomethyl radical (H_2CCN). Sumiyoshi, Yoshihiro; Tanaka, Keiichi; Tanaka, Takehiko (Fac. Sci., Kyushu Univ., Fukuoka, Japan 812–81). *J. Chem. Phys.* **1996**, 104(5), 1839–45 (Eng). The IR spectrum of the cyanomethyl radical (H_2CCN) generated by the 193 nm excimer laser photolysis of chloroacetonitrile was obsd. by time-resolved diode laser spectroscopy. About 50 lines, involving those split into doublet due to the spin–rotation interaction, were assigned to rovibrational transitions in the ν_5(CH_2–wagging) band of cyanomethyl. The mol. consts. in the ν_5 vibrational state were derived from the anal. of the obsd. wave nos., resulting in the rotational consts., A=9.095 03(21) cm^{-1}, (B+C)/2=0.335 363 4(41) cm^{-1}, and (B–C)=0.011 503 6(71) cm^{-1}, and the spin–rotation interaction const. $\epsilon_{aa} = -2.143(47) \times 10^{-2}$ cm^{-1}, where the figures in parentheses are 2.5 std. deviations to be attached to the last digit, the consts. in the ground state being fixed to the reported values from microwave spectroscopy. The band origin detd. ν_0=663.793 98(85) cm^{-1} is consistent with the value derived from the band origin detd. ν_0–663.793 98(85) cm^{-1} is consistent with the value derived from the photo–detachment of ν_0–663.793 98(85) cm^{-1} is consistent with the value derived from the photo–detachment spectroscopy and the H_2CCN^- anion. Large changes in the rotational const. A and the centrifugal distortion const. Δ_K on vibrational excitation from the ground state to the ν_5 state are accounted for by the a–type Coriolis interaction of the ν_5 vibrational state with the ν_8 (CH_2–rocking) and V_9(in–plane /ccn–bending) vibrational states.

(ν_5)

C.A. 1996, 124 N10

H_2CCN

1996

† **24Б1733. Инфракрасная полупроводниковая лазерная спектроскопия с разрешением во времени полосы ν_5 радикала цианометила (H_2CCN).** Time-resolved infrared diode laser spectroscopy of the ν_5 band of the cyanomethyl radical (H_2CCN) / Sumiyoshi Yoshihiro, Tanaka Keiichi, Tanaka Takehiko // J. Chem. Phys.— 1996.— **104**, № 5.— С. 1839–1845.— Англ.

С разрешением во времени, методом полупроводниковой лазерной спектроскопии исследована структура полосы деформационного колебания $\nu_5(CH_2)$ радикалов H_2CCN, образующихся при фотолизе хлорацетонитрила излучением (193 нм) эксимерного лазера. Получены следующие молекулярные постоянные (в см$^{-1}$): ν_0=663,794, A=9,09503, $(B+C)/2$=0,335363, $(B-C)$=0,011504, ϵ_{aa}=−2,143·10^{-2} (константа спин-вращательного взаимодействия).

В. М. Ковба

М.Л.

Х.1997, №24

$HC_{13}N$

1996

126: 81448x **Laboratory detection of the cyanopolyyne $HC_{13}N$.** Travers, M. J.; McCarthy, M. C.; Kalmus, P.; Gottlieb, C. A.; Thaddeus, P. (Division of Applied Sciences, Harvard University, Cambridge, MA 02138 USA). *Astrophys. J.* 1996, 472(1, Pt. 2), L61–L62 (Eng), University of Chicago Press. The cyanopolyyne $HC_{13}N$ was detected in the lab., and the frequency of 21 rotational transitions in the band 5–12 GHz was measured to a few parts in 10^7; correspondingly precise values for the rotational const. and centrifugal distortion const. were obtained from a least–squares fit to the data: $B_0 = 106.97258(4)$ MHz, $D_0 = 0.092(10)$ Hz (uncertainties in parentheses are 1σ in the last significant digit). The best lines for astronomical detection of this C chain, longer than any yet detected in space, probably lie in the band 5–30 GHz and can should be calcd. from B_0 and D_0 to better than 0.1 km s^{-1} in equiv. radial velocity.

Вращат.
постоян.

C.A. 1997, 126, N 6

HC_3NH (om 38597) 1996

Wang H., Cooksy A.L.,

Chem. Phys., 1996, 213, 139-57

Calculations on ground and excited state potential energy surfaces of floppy free radicals: HC_4H_2, HC_3NH, and HC_3O

HC_7N

HC_7NH^+

1997

128: 28134g **Coupled cluster calculations for HC_7N, HC_7NH^+ and C_7N, molecules of interest to astrochemistry.** Botschwina, P.; Horn, M.; Markey, K.; Oswald, R. (Institut fur Physikalische Chemie, Universitat Gottingen, D−37077 Gottingen, Germany). *Mol. Phys.* **1997**, 92(3), 381−392 (Eng), Taylor & Francis. Large−scale coupled cluster calcns. were carried out for linear HC_7N, HC_7N^+ and C_7N ($^2\Pi$ and $^2\Sigma$ states). Accurate equil. geometries (bond lengths accurate to better than 0.001 Å) are established. The ground−state rotational const. of HC_7NH^+ is predicted to be $B_0 = 553.8 \pm 0.5$ MHz. Owing to its large equil. dipole moment of 6.35 D it may be a suitable candidate for forthcoming exptl. study by microwave spectroscopy or radio astronomy. Various predictions are made for HC_7N and HC_7NH^+ to facilitate their detection by IR spectroscopy. Partially restricted open−shell coupled cluster calcns. including connected triple substitutions yield the $^2\Pi$ and $^2\Sigma$ states of C_7N to be very close in energy and substantial rovibronic interaction is expected.

теор. расчет
структур.
парамет.
м.п.

⊕

C_7N

CA 1998, 128, N3

$C_6H_4CH_3CN$

1998

Мв спектр,
A, B, C, V_0

130: 58565g **Microwave spectrum and barrier to internal rotation in ortho−tolunitrile.** Jaman, A. I.; Maiti, S.; Nandi, R. N. (Saha Inst. Nuclear Phys., I/AF, Calcutta, 700 064 India). *J. Mol. Spectrosc.* 1998, 192(1), 148−151 (Eng), Academic Press. The microwave rotational spectra of ortho−tolunitrile ($C_6H_4CH_3CN$) were studied in the ground torsional state in the frequency ranges of 22.0−26.0 GHz and 32.0−37.0 GHz. The true rotational consts. are A_r = 2890.98 MHz, B_r = 1499.75 MHz, and C_r = 993.58 MHz. A least−squares anal. of the A E splittings of 16 transitions resulted in the values of V_3 = 533.53 cal/mol and θ_a = 54.22°, assuming V_0 = 0 and I_α = 3.2 a m u. Å^2. (c) 1998 Academic Press.

C. A. 1999, 130, N5

HC_5N
HC_5N^+

1997

ab initio,
мол. пост.,
ν_i

127: 197000v **Ab initio anharmonic force fields and spectroscopic properties for HC_5N and HC_5NH^+, molecules of interest to astrochemistry.** Botschwina, P.; Heyl, Ae.; Oswald, M.; Hirano, T. (Institut fur Physikalische Chemie, Universitat Gottingen, D-37077 Gottingen, Germany). *Spectrochim. Acta, Part A* **1997**, 53A(8), 1079–1090 (Eng), Elsevier. Large-scale coupled cluster calcns. were carried out for HC_5N and HC_5NH^+. Accurate equil. geometries (~0.0005 Å accuracy) are predicted for both species. The equil. rotational const. of HC_5NH^+ is B_e = 1294.1 MHz, which should also be a good est. for the ground-state value B_o. HC_5NH^+ has a remarkably large equil. dipole moment of μ_e = 3.811 D and may thus by a suitable candidate for forthcoming study by microwave spectroscopy and radio astronomy. For HC_5N, strong anharmonic interaction is predicted between v_2 and $2v_5$ as well as between v_1 and v_3 v_5.

C.A. 1997, 127, N 14

HC_9NH^+

1997

128: 107763q **Coupled cluster calculations for HC_9NH^+, a cation of interest to astrochemistry.** Heyl, A.; Botschwina, P.; Hirano, T. (Institut fur Physikalische Chemie, Universitat Gottingen, Tammannstrsse6, D-37077 Gottingen, Germany). *J. Chem. Phys.* **1997**, 107(22), 9702-9703 (Eng), American Institute of Physics. An accurate equil. geometry was obtained for the astrochem. important cation HC_9NH^+ by coupled cluster calcns. including connected triple substitutions [CCSD(I)] and empirical corrections. The corresponding equil. rotational const. is $B_e = 286.2$ MHz. A large equil. dipole moment of $\mu_e = 9.26$ D is predicted, which should facilitate the detection of the cation by microwave spectroscopy and radio astronomy. Wave nos. for the harmonic stretching vibrations of HC_9NH+ are reported.

спектр., Di, теор. расчет

C.A. 1998, 128, N9

$(HCN)_n$

Vm. 39076

1997

Kudoh Satoshi, Masao Takayanagi et al.,

J. Mol. Struct., 1997,

413-414, 365-369.

ИК спектр
в низко-
темпер.
Ar мат
рице

$HC_{11}N$
$HC_{13}N$

1997

Mc Carthy M.C., Travers M.J. et al.,

Вращат. спектр

Astrophys. J. Suppl. Ser. 1997, 113 (1), 105-120

●

(см. C_7H и др; III)

$(HCN)_n$

1997

Кластеры

127: 167056a **Comment on "Structure and spectroscopy of $(HCN)_n$ clusters: cooperative and electronic delocalization effects in C−H−N hydrogen bonding" [J. Chem. Phys. 103, 333 (1995)].** Stone, A. J.; Buckingham, A. D.; Fowler, P. W. (Dep. Chemistry, Univ. Cambridge, Cambridge, UK CB2 1EW). *J. Chem. Phys.* 1997, 107(3), 1030−1031 (Eng), American Institute of Physics. A polemic is given on the of B. F. King and F. Weinhold (*ibid.* 1995, 103, 333) concerning structure and spectroscopy of $(HCN)_n$ clusters: cooperative and electronic delocalization effects in C−H−N hydrogen bonding.

стр-ра
и спектр

C. A. 1997, <u>127</u>, N 12

CH_2CN

1997

м/в спектр,
структурн.
параметр

127: 269635f **The microwave spectrum of the cyanomethyl radical $CH_2CN(^2B_1)$.** Saito, Shuji; Yamamoto, Satoshi (Inst. Molecular Science, Okazaki, Japan 444). *J. Chem. Phys.* **1997,** 107(6), 1732–1739 (Eng), American Institute of Physics. The rotational spectrum of the cyanomethyl radical CH_2CN in its $^2B_1$ ground electronic state was studied by microwave spectroscopy using a source-modulated spectrometer equipped with a free-space cell. The CH_2CN radical was generated in the cell by dc-glow discharge in pure MeCN, and CD_2CN in CD_3CN. Fifty a type R-branch rotational transitions were measured in the frequency region of 80 to 282 GHz, where fine structure and hyperfine structures due to the N and H nuclei were resolved for lower-N transitions, but only the fine structure for higher-N transitions. Similarly fine-structure resolved rotational transitions were measured for CD_2-CN in the frequency region of 190 to 286 GHz. The mol. consts. of CH_2-CN, including the fine-structure consts. and hyperfine coupling consts. due to both the nuclei of N and H, were precisely detd. by least-squares methods from 146 obsd. spectral lines, including 36 astronomically obsd. lines for the $K_a = 0$ components, of $N = 1-0$ and $2-1$ from a dark cloud TMC-1. Those of CD_2CN were similarly obsd. from 92 obsd. spectral lines. The rotational consts. of both the species were used to derive mol. structural parameters of CH_2CN: $r_0(CN) = 1.1919(13)$ Å, $r_0(CC) = 1.3680(12)$ Å, $r_0(CH) = 1.0894(7)$ Å on the assumption of 120.22° for $\angle$ HCH. The spin densities of unpaired electrons estd. from the hyperfine coupling consts. for the N and H atoms are consistent with the mol. structure obtained.

C. A. 1997,
127, N 19

$(HCN)_n$
$n = 2, 3$

1997

ИК спектр,
структура

127: 363630x **Infrared spectra of $(HCN)_n$ clusters in low-temperature argon matrixes.** Satoshi, Kudoh; Takayanagi, Masao; Nakata, Munetaka (Graduate School of Bio-Applications and Systems Engineering (BASE), Tokyo University of Agriculture and Technology, Saiwai-cho, Fuchu, Tokyo, Japan). *J. Mol. Struct.* **1997**, 413-414, 365-369 (Eng), Elsevier. The IR spectra of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ were measured using a low-temp. matrix isolation technique. Linear $(HCN)_2$ and cyclic $(HCN)_3$ were produced by the photolysis of s-tetrazine and s-triazine resp. Vibrational analyses of the IR bands for the C-H stretching mode and the C-N stretching and H-C-N bending modes were performed with the aid of ab initio calcns.; geometrical optimization was carried out using the d. functional theory method with a 6-31++G** basis set.

C. A. 1997, 127, N 26

C-N-H соединения (ОМ 38914) 1997

Wayner D.D.M., Clark K.B.
et al.,

До J. Am. Chem. Soc., 1997,
119, N38 √8925-32

$HCN-NC$
$HCN-CN$
$HCN-CCH$

1998

Araujo, Regiane C.M.U. et al.,

ab initio расчет

J. Braz. Chem. Soc. 1998, 9(5), 499-505

(см. $HCN-HF$; III)

HC_4NC
HC_6NC

1998

129: 222590p The isocyanopolyynes HC_4NC and HC_6NC: Microwave spectra and ab initio calculations. Botschwina, P.; Heyl, A.; Chen, W.; McCarthy, M. C.; Grabow, J.-U.; Travers, M. J.; Thaddeus, P. (Institut fur Physikalische Chemie, Universitat Gottingen, Tammannstr. 6, D-37077 Gottingen, Germany). *J. Chem. Phys.* **1998**, 109(8), 3108-3115 (Eng), American Institute of Physics. Rotational spectra of HC_4NC and HC_6NC, linear mols. of interest to interstellar cloud chem., were recorded by Fourier transform microwave spectroscopy, and the ground state rotational consts. are 1401.18227(7) and 582.5203(1) MHz.

N quadrupole hyperfine structure could be obsd. for HC_4NC. From coupled cluster calcns. including connected triple substitutions accurate equil. structures (uncertainty in bond lengths -0.0005 A) could be established for both species. The equil. dipole moments, predicted to be -3.25 and -3.49 D for HC_4NC and HC_6NC, resp., exhibit large correlation effects of 30 and 33%.

МВ спектр +
ab initio
расчет

C. A. 1998, 129, N17

$CH_3(C:C)_nCN$

n=2-5

1998

130: 73140h **Microwave spectra of the methylcyanopolyynes $CH_3(C:C)_nCN$, n = 2, 3, 4, 5.** Chen, Wei; Grabow, J.–U.; Travers, M. J.; Munrow, Michaeleen R.; Novick, Stewart E.; McCarthy, M. C.; Thaddeus, P. (Harvard–Smithsonian Cent. Astrophys., Cambridge, MA 02138 USA). *J. Mol. Spectrosc.* **1998**, 192(1), 1–11 (Eng), Academic Press. The ground state rotational spectra of four methylcyanopolyynes $CH_3(C:C)_2CN$, $CH_3(C3C)_3CN$, $CH_3(C:C)_4CN$, and $CH_3(C:C)_5CN$ were measured between 6 and 22 GHz by Fourier transform microwave spectroscopy. For $CH_3(C:C)_2CN$, previously obsd. by Alexander et al. [J. Mol. Spectrosc. **70**, 84–94(1978)] eight transitions were obsd., each with sufficient resoln. to det. the N quadrupole hyperfine const. for the 1st time: eqQ = −4.25(3) MHz. The longer three methylcyanopolyynes are new; for these, from 10 to 21 rotational transitions were detected and precise values for the rotational and the leading centrifugal distortion consts., and eqQ for CH_3 $(C3C)_3CN$, were detd. (c) 1998 Academic Press.

(МВ спектр)

C.A. 1999, 130, N6

H_2 CCCCN

1998

128: 210216n **Laboratory detection of a new carbon chain radical: H_2CCCCN.** Chen, Wei; Mccarthy, M. C.; Travers, M. J.; Gottlieb, E. W.; Munrow, Michaeleen R.; Novick, Stewart E.; Gottlieb, C. A.; Thaddeus, P. (Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138 USA). *Astrophys. J.* **1998**, 492(2, Pt. 1), 849–853 (Eng), University of Chicago Press. $\cdot H_2CC{\vdots}CC{\vdots}N$ was detected in a supersonic mol. beam by Fourier transform microwave spectroscopy. For the normal and ^{15}N species, 89 and 40 hyperfine components, resp., from 4 successive rotational transitions ($N = 2 \rightarrow 1$ to $5 \rightarrow 4$) in the lowest energy ($K_a = 0$) rotational ladder were measured at 8–22 GHz to an uncertainty of 5 kHz. With this data, the microwave consts. of $\cdot H_2CC{\vdots}CC{\vdots}N$, including the fine and hyperfine coupling consts., are detd. to high accuracy, and the most interesting lines in the radio spectrum from an astronomical standpoint can now be calcd. to a fraction of 1 km s^{-1} in equiv. radial velocity.

FTmW спектр

C.A. 1998, 128, N 17

Метиламин,
диметиламин

C-N-H.

1998

ab initio
расчет,
ИК спектр.

130: 116581x Ab initio determination of band structures of vibrational spectra of non-rigid molecules. Applications to methylamine and dimethylamine. Smeyers, Y. G.; Senent, M. L.; Villa, M. (Instituto de Estructura de la Materia, C.S.I.C., Madrid, Spain E-28006). *Adv. Quantum Chem.* **1998**, 32, 145-166 (Eng), Academic Press. The ab initio detn. of the band structures of IR spectra is described giving as examples the Me torsion and amine wagging in methylamine and the double torsion in dimethylamine. The influence of the amine H sym. bending and the CNC skeleton sym. bending is considered in methylamine and dimethylamine, resp. For this purpose, the potential energy surfaces and kinetic parameters are detd. at the RHF/MP2 levels with large basis sets. The numerical results are fitted as a function of the vibrational angles to conveniently symmetry adapted functional forms.

C.A. 1999, 130, N9

The Schroedinger equations for the nuclear motions solved by expanding the solns. into products of trigonometric functions. From the energy levels, the vibrational functions and the elec. dipole moment variations the bands locations and intensities are detd. The calcd. spectra are compared with the available exptl. data. In the case of methylamine, the torsional splittings and frequencies are relatively well reproduced, whereas the wagging frequencies appear to be slightly too high. In the case, of dimethylamine, the sym. and antisym. torsion modes are very well reproduced, whereas the CNC bending frequencies appear also to be too high.

CH_3N_3 (От. 39400) 1998

Wang Zhizhong,

геометр.,
колебат.
частоты,
ab initio
расчет

J. Mol. Struct.
(Theochem) 1998, <u>434</u>, 1-5.

1999

F: (HCN)n-
P: 3
130:257555 Electron binding energies in linear dipole-bound (HCN)n- (n=2- anions. Gutowski, Maciej; Skurski, Piotr (Materials and Chemical Sciences Pacific Northwest National Laboratory, Richland, WA 99352, USA). Chem. P Lett., 300(3,4), 331-338 (English) 1999 The (HCN)2- anion was studied at the coupled cluster level of theory wit single, double, and non-iterative triple

excitations whereas equil. struc and electron binding energies for larger linear (HCN)n- (n=3-5) clusters detd. at the second-order Moller-Plesset (MP2) level. The adiabatic elec affinity of (HCN)2 was found to be 399 cm-1 and trends in phys. meaningfu components of electron binding energy, such as static Coulomb, dispersion polarization stabilizations, were detd. for this series of clusters. The dipole-bound anionic state was found for the pentamer with the MP2 vertic electron detachment energy of 92 cm-1.

HC_4N От. 40168 1999

спектр,

м.п.

Jian Tang, Yoshihiro Sumiyoshi, Yasuki Endo,

Chem. Phys. Lett.,
1999, <u>315</u>, 69-74

HC_4N
HC_6N

1999

131: 51437d **Laboratory detection of the ring–chain carbenes HC_4N and HC_6N.** McCarthy, M. C.; Grabow, J.–U.; Travers, M. J.; Chen, W.; Gottlieb, C. A.; Thaddeus, P. (Harvard–Smithsonian Center for Astrophysics, Cambridge, MA 02138 USA). *Astrophys. J.* **1999**, 513(1, Pt. 1), 305–310 (Eng), University of Chicago Press. The highly polar ring–chain carbenes HC_4N and HC_6N, formed by substituting either CN or CCCN for a H atom in cyclopropenylidene (c–C_3H_2), were detected in a supersonic mol. beam with a Fourier transform microwave spectrometer. Seven a– and 4 b–type rotational transitions of HC_4N and 11 a–type transitions of HC_6N, each with resolved N nuclear quadrupole hyperfine structure, were measured between 6 and 21 GHz, yielding precise values for the 3 rotational consts.; the leading centrifugal distortion consts., and the quadrupole coupling consts. Like the hydrocarbon carbenes C_5H_2, C_7H_2, and C_9H_2, both new mols. have a planar ring–chain structures and singlet electronic ground states. The strongest lines of HC_4N can be detected with a signal–to–noise ratio exceeding 10 in a total integration time of <1 s, but the lines of HC_6N were nearly 100 times weaker.

(N 6 ИК
(спектры)

C.A., 1999, 131, N4.

OM 39910 1999

F: HC4N
P: 3
132:16656 Rotational spectrum and theoretical structure of the carbene HC McCarthy, M. C.; Apponi, A. J.; Gordon, V. D.; Gottlieb, C. A.; Thaddeus P.; Daniel Crawford, T.; Stanton, John F.
Harvard-Smithsonian Center for Astrophysics
Cambridge, MA 02138, USA J. Chem. Phys., 111(15), 6750-6754 (English) 1999

Following a high-level coupled cluster calcn., the rotational spectrum o the bent HC4N

C. A. 2000, 132

singlet carbene was detected in a supersonic mol. beam by F. transform microwave spectroscopy. The three rotational consts., the lead centrifugal distortion consts., and two N hyperfine coupling consts. high accuracy. The rotational consts. agree with those calcd. ab initio to be than 0.5%. Like the isoelectronic C5H2 carbene of similar structure, HC4 fairly large centrifugal distortion and a large inertial defect. The cal dipole moment of HC4N is 2.95 D.

F: HC4N
P: 3

1999

132:16656 Rotational spectrum and theoretical structure of the carbene HC4N. McCarthy, M. C.; Apponi, A. J.; Gordon, V. D.; Gottlieb, C. A.; Thaddeus, P.; Daniel Crawford, T.; Stanton, John F.
Harvard-Smithsonian Center for Astrophysics
Cambridge, MA 02138, USA J. Chem. Phys., 111(15), 6750-6754 (English) 1999 Following a high-level coupled cluster calcn., the rotational spectrum of the bent HC4N singlet carbene was detected in a supersonic mol. beam b Fourier transform microwave spectroscopy. The three rotational consts., leading centrifugal distortion consts., and two N hyperfine coupling cons high accuracy. The rotational consts. agree with those calcd. ab initio better than 0.5%. Like the isoelectronic C5H2 carbene of similar structu HC4N has fairly large centrifugal distortion and a large inertial defect. The calcd. dipole moment of HC4N is 2.95 D. HC4N

C.A. 2000, 132

C_4H_5N

1999

130: 145548x **Rotation–vibration constants for the ν_1, ν_{22}, ν_{24}, $\nu_{22} + \nu_{24}$, and ground states in pyrrole ($^{12}C_4H_5N$).** Mellouki, Abdeloihid; Auwera, Jean Vander; Herman, Michel (Laboratoire de Chimie Physique Moleculaire, Universite Libre Bruxelles, 1050 Brussels, Belg.). *J. Mol. Spectrosc.* 1999, 193(1), 195–203 (Eng), Academic Press. The IR spectrum of pyrrole was recorded at 0.005 cm^{-1} spectral resoln. using a Fourier transform interferometer. The rotational anal. of the sym. out-of-plane C–H bend 22_0^1 fundamental band at 722.132993(5) cm^{-1} was performed, allowing 6760 lines to be assigned. These lines were fitted simultaneously to literature data on ν_1 (Mellouki, A., et al., 1997) and microwave lines (Wlodarczak, G., et al., 1988). A set of rotation parameters was detd. for the ground state in I' and III' representations, together with vibration–rotation consts. for the $\nu_1 = 1$ and $\nu_{22} = 1$

(Vi)

C. A. 1999, 130, N 11

vibrational states. The fine structure in the strongest of the hot bands in that range was highlighted by division, from the exptl. data, of the spectrum of the 22_0^1 band, computed using the vibration–rotation parameters. The rotational assignment of 930 lines in the strongest hot band was performed. The $22_0^1 24_1^1$ vibrational assignment is proposed, leading to $x_{22,24} = 1.90$ cm^{-1}. The transition dipole matrix element for the 22_0^1 band is estd. to $|\langle \psi'_{22} | \mu_c | \psi'_0 \rangle| = 2 \times 10^{-4}$ D. (c) 1999 Academic Press.

F: HC3NH+

P: 3

1999

132:180217 Ion-molecule reactions producing HC3NH+ in interstellar space. Forbiddenness of the reaction between cyclic C3H3+ and the N atom.

Takagi, Nozomi; Fukuzawa, Kaori; Osamura, Yoshihiro; Schaefer, Henry F. III Department of Chemistry, Tokyo Metropolitan University Tokyo 192- 0397, Japan Astrophys. J., 525(2, Pt. 1), 791-798 (English) 1999 The reaction between cyclic C3H3+ and the N atom is thought to be a key element in the synthesis of the interstellar mol. HC3N, which is the most abundant species in the cyanopolyyne series in dark clouds. We have exam the potential energy surfaces for the reaction between cyclic C3H3+ and t atom using ab initio

C. A. 2000, 132

quantum mech. methods to confirm whether this reacti is feasible in interstellar space. The potential energy surface between cyclic C3H3+ and the ground-state N atom is, however, predicted to be repulsive. The reaction between cyclic C3H3+ and the N atom ground state (4S) is concluded not to produce HC3NH+ in interstellar space, in addn. t the fact that this reaction is spin-forbidden. The alternative pathway t produce HC3NH+ is the reaction between HCCH+ and HCN. This reaction is f to be very crit. for the prodn. of HC3NH+ and the H atom because this pro requires several reaction steps in a complicated unimol. rearrangement an must go through an energy barrier which is very close to the energy of th reactants. The other possible way to produce HC3NH+ is shown to be the reaction between HCCH+ and HNC. The theor. potential energy surface sugg that the HCCNCH+ isomer of HC3NH+ cannot be formed from HCCH+ + HCN becau of the endothermicity and the high energy barrier for this process. The present study supports the view that the ion-mol. reactions are not a significant source for the prodn. of the HC3NH+, and therefore of the HC3 mol. in interstellar space. The probable pathways to form HC3NH+ are the reaction HCCH+ + HNC and the protonation of HC3N, produced mainly via neutral-neutral reactions.

F: HC4N
P: 3

1999

132:151439 Detection of the triplet HC4N radical by Fourier transform microwave spectroscopy. Tang, J.; Sumiyoshi, Y.; Endo, Y. Meguro-ku, Koma 3-8-1, Department of Basic Sciences, The University of Tokyo Tokyo, Japan Chem. Phys. Lett., 315(1,2), 69-74 (English) 1999 The triplet HC4N radical in a linear C-chain form was detected by Fourier transform microwave spectroscopy for the 1st time. Rotational transitions with fine and hyperfine structures, ~ 130 lines in total, were obsd. in a pulsed-discharge-nozzle supersonic expansion of the HC3N sample dild. in Ar buffer gas. The spectrum was assigned to the linear HC4N radical by various combinations of discharge gases, by the rotational, fine and hyperfine structures, and most decisively, by comparison of the detd. mol. consts. with those of the HCCN radical.

C.A. 2000, 132

F: $CH3CNH^+$
P: 3

2000

133:302714 Accurate Equilibrium Structures and Equilibrium Dipole Moments for CH3CNH+ and CH3C3NH+. Botschwina, Peter Institut fur Physikalische Chemie Gottingen D-37077, Germany J. Mol. Spectrosc., 203(1), 203-204 (English) 2000. Ab initio calcns. of CH3CNH+ and CH3C3NH+ were performed and the results were presented. Five different methods with five different basis set were used for each compd. Calcd. equil. bond lengths, total energies and equil. rotational consts. as well as equil. elec. dipole moments were presented.

F: Pyridine C_5H_5N 2000
P: 3

133:288248 The Low-Lying Excited States of Pyridine. Cai, Zheng-Li; Reimers, Jeffrey R. School of Chemistry, University of Sydney 2006, Australia
J. Phys. Chem. A, 104(36), 8389-8408 (English) 2000

The authors assign the obsd. phosphorescence and high-resoln. singlet-to-triplet absorption spectra of pyridine, performing large model vibronic coupling calcns. involving 6 active modes and 3 near-degenerate electronic states, 3A1, (2)3A1, and 3B1. Vibronic coupling primarily through .nu.8a between 3A1 and (2)3A1 results in the breakdown of the pseudo-parity selection rule: the lower surface has a double min., with each well corresponding to a diabatic single-determinant (.pi.,.pi.*)

excitation. These states then strongly vibronically couple to 3B1 primarily through .nu.16b, resulting in a very complex 3A' manifold. In addn., for the singlet manifold, the authors detail a low-lying conical intersection between 1B1 and 1A2 and suggest that this intersection should have observable consequences for excited-state dynamics. These conclusions are obtained through the examn. of all states <5 eV in energy [1B1 (S1), 1B2 (S2), 1A2 (S3), 3A1, (2)3A1, 3B1, 3A2, and 3B2], performing CIS, CASSCF, CASPT2, CCSD, CCSD(T), EOM-CCSD, CNDO/S, B3LYP, BLYP, TD-B3LYP, and TD-BLYP calcns. for the vertical excitation and emission energies; equil., transition-state, and conical-intersection structures; vibration frequencies; spin-orbit couplings; vibronic couplings; ESR at. spin densities; and low-resoln. absorption and emission band contours. Special techniques are developed for the application of the electronic structure methods to the evaluation of the required mol. properties, and the application of a wide range of methods is required both because of the diversity of the required properties and because the intrinsic errors in the methods are of magnitudes that are chem. significant.

F: $CH_2(NH_2)_2$
P: 3

2000

133:321950 Ab Initio Study and NBO Interpretation of the Anomeric Effect in $CH_2(XH_2)_2$ (X = N, P, As) Compounds. Carballeira, Luis; Perez-Juste, Ignacio Departamento de Quimica Fisica Facultad de Ciencias, Universidad de Vigo Vigo, Spain J. Phys. Chem. A, 104(41), 9362-9369 (English) 2000. The generalized anomeric effects in nitrogen, phosphorus, and arsenic compds. were examd. in detail by means of ab initio calcns. The conformational preferences can be considered adequately described at the HF/6-311G**//MP2/6-311G** level, since these results agree with those obtained using larger basis sets and including electron correlation up to the MP4 level. The favored conformers show two or one anti orientations between the X lone pair (Lp-X) and the

X-C polar bond. According to the NBO anal. of the Hartree-Fock wave functions, the preferences for the anti Lp-X-C-X orientations and the barriers to internal rotation are due mainly to charge delocalization, which is always stronger than the electrostatic and steric contributions included in the Lewis term. These features are much larger for second-row substituents. From the comparison with the previously reported data for the corresponding oxygen, sulfur, selenium, and tellurium compds., an increase of the stability of the conformers favored by anomeric orientations and also of the rotational barriers can be obsd. from group 15 to group 16 of the periodic table. The reason for this fact, more noticeable for second-row compds., is the predominant role of the Lewis energy, i.e., the non- hyperconjugative contributions. The calcd. energies for the group sepn. reactions also increase when moving to the right through the periodic table, but they are not a reasonable measurement of the generalized anomeric effect, since they do not have a direct relationship with the conformational preferences.

$NH_3CH_3^-$ 2000

Hopper Hugh; et al.,

J. Am. Chem. Soc., 2000,
<u>122</u> (51), 12813-18.

стабильн.,
структура,
Ae, теор.
расчет

(См. ● NH_3OH^-; III)

HC_4N, HC_6N (стабильн., структура мол. расчет) 2000

134: 9635d The most stable isomers in HC_4N and HC_6N. Ikuta, S.; Tsuboi, T.; Aoki, K. (Graduate School of Engineering, Tokyo Metropolitan University, Tokyo, Japan 192−0397). *THEOCHEM* **2000**, 528, 297−305 (Eng), Elsevier Science B.V. The relative stability of the triplet−linear A to the singlet B with a C_3−ring in an HC_4N mol. was investigated at the d. functional level of theory with Becke's three parameters (B3LYP) and the coupled−cluster singles and doubles with triple contributions (CCSD(T)). The various qualities of the correlation−consistent basis sets were used. After the zero−point vibrational energy corrections, the singlet B is by 4.2 kcal/mol lower in energy than the triplet A at the present highest level of theory (CCSD(T)/cc−pCVTZ with core electron correlations (CCSD(T)(full)/cc−pCVTZ)). The B3LYP calcns. failed to predict the relative stability, however, the optimized geometries even with the cc−pVDZ basis set are in good agreement with the accurate CCSD(T)/cc−pVTZ ones. For the larger HC_6N mol., the CCSD(T)/cc−pVTZ and cc−pCVDZ energy calcns. (with and without core electron correlations) on the basis of the B3LYP optimized parameters were performed to predict the relative stabilities of the triplet−linear C to the two singlet−rings (D and E). The triplet C is the most stable isomer, which are by 2.4 and 4.0 kcal/mol lower in energy than the singlets D and E, resp., after the corrections due to the zero−point vibrational energies.

HC_6N (стабильн., стр-ра, теор. расчет)

2000

134: 9635d **The most stable isomers in HC_4N and HC_6N.** Ikuta, S.; Tsuboi, T.; Aoki, K. (Graduate School of Engineering, Tokyo Metropolitan University, Tokyo, Japan 192−0397). *THEOCHEM* 2000, 528, 297−305 (Eng), Elsevier Science B.V. The relative stability of the triplet−linear A to the singlet B with a C_3−ring in an HC_4N mol. was investigated at the d. functional level of theory with Becke's three parameters (B3LYP) and the coupled−cluster singles and doubles with triple contributions (CCSD(T)). The various qualities of the correlation−consistent basis sets were used. After the zero−point vibrational energy corrections, the singlet B is by 4.2 kcal/mol lower in energy than the triplet A at the present highest level of theory (CCSD(T)/cc−pCVTZ with core electron correlations (CCSD(T)(full)/cc−pCVTZ)). The B3LYP calcns. failed to predict the relative stability, however, the optimized geometries even with the cc−pVDZ basis set are in good agreement with the accurate CCSD(T)/cc−pVTZ ones. For the larger HC_6N mol., the CCSD(T)/cc−pVTZ and cc−pCVDZ energy calcns. (with and without core electron correlations) on the basis of the B3LYP optimized parameters were performed to predict the relative stabilities of the triplet−linear C to the two singlet−rings (D and E). The triplet C is the most stable isomer, which are by 2.4 and 4.0 kcal/mol lower in energy than the singlets D and E, resp., after the corrections due to the zero−point vibrational energies.

$C_4H_9NH_2$ и др.

Оп. 40533

2000

Jie Cao et al.,

Ap J. Phys. Chem. 2000, A104,
10045 - 10052.

Proton Affinities ~~of~~ Simple
Amines; Entropies and En—

thalpies of Activation and
Their Effect on the Kinetic
Method for Evaluating
Proton Affinities

2000

F: C4H5N
P: 3
132:293450 Multiphoton ionization and ab initio calculation studies of the hydrogen-bonded clusters C4H5N-(H2O)n. Li, Yue; Hu, Yongjun; Liu, Xianghong; Wang, Xiuyan; Lou, Nanquan State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023, Peop. Rep. China
Xuebao, 13(1), 11-19 (Chinese) 2000

The multiphoton ionization of the

C.A. 2000

hydrogen-bonded clusters C4H5N-(H2O)n was studied using a time-of-flight mass spectrometer at 355 nm and 532 nm laser wavelengths. At both wavelengths, a series of C4H5N- (H2O)n+ and the protonated products C4H5N-(H2O)n.H+ were obtained. The two-photon resonance ionization processes at 355 nm make the ion intensities of pyrrole and the clusters obviously more abundant than at 532 nm. Ab initio calcns. show that in the protonated products, the proton prefers to link with .alpha.-C of pyrrole rather than with the N atom. The prodn. of the protonated products needs an intracluster proton transfer reaction. The protonated products obtained at 532 nm are suggested to arise from an intracluster Penning ionization or a charge transfer process. The abnormally higher intensities of photofragments C4H4N-(H2O)n+ (n.gtoreq.1) than C4H4N+ are attributed to the stabilization effects of the cluster formation on the dissocn. products C4H4N+ of the pyrrole mol.

2000

F: HC7N
P: 3
133:302790 Experimental Structures of the Carbon Chains HC7N, HC9N, and HC11N by Isotopic Substitution. McCarthy, M. C.; Levine, E. S.; Apponi, A. J.; Thaddeus, P. Harvard-Smithsonian Center for Astrophysics Cambridge, MA 02138, USA J. Mol. Spectrosc., 203(1), 75-81 (English) 2000. The effective structures of the 3 linear cyanopolyynes HC7N, HC9N, and HC11N have been detd. to high accuracy by isotopic substitution, following detection in a supersonic mol. beam with a Fourier transform microwave spectrometer of all of the singly substituted rare isotopic species.

For each chain, the lengths of the individual bonds have been detd. to an accuracy of 0.001 A or 0.1% toward the end of the chain and to 0.01 A or 1.0% toward the center. The exptl. structures are in excellent agreement with recent high-level theor. calcns., or, in the case of HC11N, with extrapolation from HC9N. The three polyynes studied here represent the largest reactive carbon chain mols. for which accurate structures have been derived empirically. For HC7N and HC9N, it has been possible to resolve at high-resoln. nitrogen hyperfine structure in the lower rotational transitions and det. eQq for all of the singly substituted isotopic species of HC7N and for normal HC9N.

2000

F: CH3N3
P: 3
133:50329 Vibrational frequencies of hydrazoic acid and methyl azide: density functional theory study. Zhou, Zheng-Yu; Du, Dong- Mei; Fu, Ai-Ping; Yu, Qing-Sen Department of Chemistry, Qufu Normal University Shandong 273165, Peop. Rep. China
Chin. J. Chem., 18(3), 297-302 (English)

C. A. 2000

[illegible] Harmonic vibrational frequencies of HN3 and MeN3 mols. and their several isotopomers are calcd. using HF, MP2 and 5 popular d. functional theory (DFT) methods. From the comparison between calcd. and exptl. results, assignments of fundamental vibrational modes are examd. HF and MP2 results are in bad agreement with exptl. values. Of the 5 DFT methods, BLYP reproduces the obsd. fundamental frequencies the most satisfactorily. Two hybrid DFT methods yield frequencies generally higher than the obsd. fundamental frequencies. BLYP calcn. is a very promising approach for understanding the obsd. spectral features. [illegible]

$C_6H_7N^+$

[illegible] 2001

(Vi, UK)

135: 128941f **Infrared spectroscopy of aniline ($C_6H_5NH_2$) and its cation in a cryogenic argon matrix.** Gee, C.; Douin, S.; Crepin, C.; Brechignac, P. (Laboratoire de Photophysique Moleculaire, Universite Paris–Sud, F–91405 Orsay, Fr.). *Chem. Phys. Lett.* 2001, 338(2,3), 130–136 (Eng), Elsevier Science B.V. IR absorption spectra of aniline, trapped in a low–temp. 5 K Ar matrix, were obtained in the spectral region from 500 to 4000 cm^{-1}. The aniline cation $C_6H_7N^+$, was formed inside the matrix by UV laser irradn. The authors report the 1st IR absorption spectroscopy of this cation in an Ar matrix: five fundamental vibrational bands were obsd.

C.A. 2001, 135, N9

Алкил - нитраты

2001

(До)

135: 247813a Efficient energies of interaction of functional groups and energies of dissociation bonds in alkylnitrates. Kostikova, Larissa M.; Miroshnichenko, Evgeniy A.; Inozemtcev, Jaroslav O.; Matyushin, Yuriy N. (Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia 117977). *Int. Annu. Conf. ICT* 2001, 32nd(Energetic Materials), 104/1–104/9 (Eng), Fraunhofer-Institut fuer Chemische Technologie. The enthalpies of formation of mono- and polyalkylnitrates in the std. condition are recommended on

C.A. 2001, 135, N17

the basis of our exptl. data and anal. of literary values. The contributions of the nitrate groups in the enthalpy characteristics of the alkylnitrates are obtained. The energy effects of interaction of nitrate groups in the gas phase are detd. The calcd. bond dissocn. energies of the alkylnitrates are compared with the those of the corresponding alcs.

HC_6N Om. 40763 2001

Olga Vaizert et al.,

$A^3\Sigma^- - X^3\Sigma^-$

J. Chem. Phys., 2001,
114, N 18, 7918 – 7922

The $A^3\Sigma^- - X^3\Sigma^-$ electronic transition of HC_6N.

para – H_2C_4N 2001

135: 202116j Laboratory observation of para–H_2C_4N. Tang, Jian; Sumiyoshi, Yoshihiro; Endo, Yasuki (Department of Basic Sciences, University of Tokyo, Tokyo, Japan 153–8902). *Astrophys. J.* 2001, 552(1, Pt. 1), 409–412 (Eng), University of Chicago Press. The rotational spectrum of para–H_2C_4N ($I(H) = 0$) in the $K_a = 1$ rotational level was obsd. in supersonic expansion at low temp. by Fourier transform microwave spectroscopy. The C_{2v} structure of H_2C_4N was confirmed by an anal. of both the present $K_a = 1$ transitions and the $K_a = 0$ transitions from the previous ortho–H_2C_4N ($I(H) = 1$) study. Rest transition frequencies of para–H_2C_4N are now available for radio–astronomical searching.

МВ спектр, стр-ра C_{2v}

C.A. 2001, 135, N9.

HC_6N 2001

135: 144103q The $A^3\Sigma - X^3\Sigma-$ electronic transition of HC_6N. Vaizert, Olga; Motylewski, Tomasz; Wyss, Muriel; Riaplov, Evgueni; Linnartz, Harold; Maier, John P. (Institute for Physical Chemistry, CH−4056 Basel, Switz.). *J. Chem. Phys.* 2001, 114(18), 7918−7922 (Eng), American Institute of Physics. A combined matrix and gas phase study is presented to identify the $A^3\Sigma^- - X^3\Sigma^-$ electronic transition of the linear triplet isomer of HC_6N and isotopic deriv. DC_6N. Absorption spectra were obsd. in a 6 K Ne matrix after mass selective deposition and in the gas phase by cavity ring down spectroscopy through a supersonic planar plasma. The band origin of the 0_0^0 $A^3\Sigma^- - X^3\Sigma^-$ electronic transition of HC_6N is at 21208.60(5) cm^{-1}, shifted ~30 cm^{-1} to the blue of the Ne matrix value. Rotational anal. indicates that the chain is slightly stretched on electronic excitation, yielding $B_0'=0.02792(5)$cm^{-1}. Transitions to vibrationally excited levels in the upper $A^3\Sigma^-$ state are obsd. as well. The results are compared with a rotationally resolved spectrum of the 0_0^0 $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic transition of the isoelectronic HC_7H species.

$(A^3\Sigma - X^3\Sigma^-)$
линейная
мол-ла,
м.л.

C.A.2001, 135, N10

Methyl Nitrite

2001

(ИК в матрице)

ΔH_f и др.

135: 233175g Conformational Characteristics of Methyl Nitrite: A Cryospectroscopic Study. van der Veken, Benjamin J.; Herrebout, Wouter A. (Department of Chemistry, Universitair Centrum Antwerpen, B2020 Antwerpen, Belg.). *J. Phys. Chem. A* 2001, 105(30), 7198–7204 (Eng), American Chemical Society. Mid–IR spectra of solns. in liq. Ar, Kr, and Xe of Me nitrite, which occurs as a mixt. of cis and trans conformers, were studied. In liq. Ar and in liq. Kr at temps. <150 K, the rate of conformational equilibration is negligible, while at temps. >160 K in liq. Kr, and in liq. Xe, the equilibration is near–instantaneous. The std. enthalpy difference ΔH° between the conformers in liq. Kr was measured in the 165–205 K interval to be 3.02(9) kJ mol^{-1}, with the cis as the more stable conformer. Starting from solns. contg. nonequil. populations of the conformers, the conformational equilibration was

C.A. 2001, 135, N16.

studied as a function of time at 5 different temps. between 150 and 160 K in liq. Kr. From these kinetic data, the extinction coeff. ratios for the ν_3 and ν_8 conformational doublets are 1.2(2) and 4.8(8), resp. The extinction coeff. ratio for ν_8 was combined with the value for ΔH° to yield the value of 5.1(2) J K^{-1} mol^{-1} for the std. conformational entropy difference ΔS°. The kinetic data also were used to calc. the enthalpy and entropy of activation for the interconversion from trans to cis conformer, and are 44.0(14) kJ mol^{-1} and 16(9) J K^{-1} mol^{-1}, resp. The results are discussed in light of literature data and in light of perturbation Monte Carlo calcns. on solvation enthalpy and entropy.

C_3H – HCN
C_2H_4 – HCN
C_2H_2 – HCN

2001

135: 200687x **An ab initio study of the structural and vibrational properties of the C_3H_6–HCN, C_2H_4–HCN and C_2H_2–HCN hydrogen–bonded complexes.** Lopes, K. C.; Pereira, F. S.; de Araujo, R. C. M. U.; Ramos, M. N. (Departamento de Quimica, Universidade Federal da Paraiba, 58036–300 Joao Pessoa (PB), Brazil). *J. Mol. Struct.* **2001**, 565–566, 417–420 (Eng), Elsevier Science B.V. MP2/6-311++G^{**} ab initio MO calcns. were performed to obtain the mol. properties of the C_3H_6–HCN, C_2H_4–HCN and C_2H_2–HCN H–bonded complexes. The more pronounced effects on the structural parameters of the isolated mols. due to complexation are verified by the CC and H–CN bond lengths which are directly involved in the H–bond formation; these

ab initio
расчет,
стр-ра, стаб;
частоты
колебаний

C.A. 2001, 135, № 14

increase after complexation. The calcd. H−bond lengths are in excellent agreement with the exptl. ones. The H−bond energies after inclusion of the zero−point contributions are −8.7, −7.6 and −9.0 kJ mol^{-1} for the C_2H_2−HCN, C_2H_4−HCN and C_3H_6−HCN complexes, resp. These values are in very good agreement with the approx. exptl. binding energies obtained from the well depth using a Lennard−Jones 6−12 potential. The more pronounced effect on the normal modes of the isolated mols. after complexation occurs in the H−X stretching mode. The H−X stretching frequency is shifted downward whereas its IR intensity is much enhanced upon H−bond formation.

$HCCNN^+$ От. 41022 ! 2001

Yi-Hong Ding* et al.,

стр-ра,
стабильн.,
теорет.
расчет

J. Phys. Chem., 2001,
A105, 7085-7090.

Theoretical Study on
Structures and Stability

of $HCCNN^+$ Isomers.

C_6H_5N, 41975 2003

$C_6H_5N_3$ Che Huijuan et all.

Chem. Phys. Letters, 2003, 382, p. 291-296

[Первое определение энергии ионизации фенил нитрила $P.RN_3$]

есть только 1-я стр. !

III к