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Prediction of R–H Homolytic Bond Dissociation Energies from Gas–Phase IR Data on ν_{CH} Values[#]

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Abstract

The main goal of this work is the application of ν_{CH} IR frequencies of gaseous R–H molecules to thermochemistry of carbon–centered R• free radicals. For the first time the variable $\Delta\nu_{CH}$ (in R–H molecules) per 1 kcal mol^{-1} in bond dissociation energies are suggested: 9 cm^{-1} for alkanes, 11 cm^{-1} for C–H bond in alkenes, 12 cm^{-1} in RC≡C–H and 14 cm^{-1} for RC$\underline{H}$=O molecules. This being accepted the exact ΔH_f^0 values for several key aliphatic free radicals (Me_3C•, •CH_2OH, •CH_2NH_2, •CH_2NHMe, •CH_2NMe_2) and the novel values for 12 substituted ethynyl RC≡C• radicals are suggested. For the latter, the specific role of polarizability of substituent R in stabilization of radical center is demonstrated. The limitations and difficulties in application of IR spectra to free radicals' thermochemistry are analyzed. The absence of low lying ("adiabatic") C–H bond in many CH_3X molecules and the observation of these bonds at much (by 60–180 cm^{-1}) higher frequencies compared with expected ones makes questionable the application of IR spectra to these purposes. However, the small deviations by 20–40 cm^{-1} can be well treated by isodesmic reactions control and Raman spectra for prediction of "lost" frequency and ΔH_f^0 of free radical as it was demonstrated for •CH_2OCH_3 and Me_3CCH_2• radicals.

Keywords. Thermochemistry; free radicals; IR spectroscopy; isodesmic reactions.

1 INTRODUCTION

Despite the obvious importance of knowledge of accurate values of the enthalpies of formation of free radicals for synthesis, chemical kinetics, chemistry of atmosphere and combustion, biochemistry, spectroscopy considerable uncertainty about these values remains. The range of known values for many of them is large and no tendency is observed to make this range narrower. For example, this range for vinyl C_2H_3• free radical encompasses 63.0 to 75.7, for ethynyl HC≡C• 110.4 to 139, for cyanoethynyl N≡CC≡C• 132 to 178.2, for •COOH –44.7 to –62.6, C_6F_5• –89.7 to

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–143.2, $Me_3Si\bullet$ –25.1 to +14.9, $PH_2\bullet$ 22 to 39, for $AlH_2\bullet$ 40 to 71 kcal mol^{-1} ([1–5] and references therein). Even for Et•, $Me_2CH\bullet$, $Me_3C\bullet$, $Me_3CCH_2\bullet$ alkyl free radicals there is no common opinion about their enthalpies of formation [2].

Recently ([1–5] and references therein) the general procedure of the series of isodesmic reactions has been elaborated for checking the known values and correcting or finding novel values of the enthalpies of formation for free radicals. Here, we further present the application of this methodology to thermochemistry of free radicals this time for analysis of gas phase $\nu_{C\underline{H}}$ isolated frequencies in gas phase IR spectra of R–H molecules and its correlation with the relative thermodynamic stabilities of R• free radicals. The correlation of stretching frequencies with chemical and physical properties is a popular and sometimes instructive occupation. In many works the correlations between isolated $\nu_{C\underline{H}}$ frequencies (in $RC\underline{H}D_2$, $RC\underline{H}DR'$ and $R(R')(R'')C\underline{H}$ molecules with C–H bond dissociation energies (BDEs) have been performed ([6-13] and references therein). For a number of reasons a reexamination of these correlations is now timely.

2 POSITIVE RESULTS

Earlier, to derive the BDE values from $\nu_{C\underline{H}}$ data the unique ratio 11 cm^{-1} in Δν equivalent to 1 kcal mol^{-1} of ΔBDE was applied for *all* types of C–H bonds [6]. In present work we propose for the first time the variable values for this interrelationship which depend on electronegativity (EN) of C–atom [1,5].

$$C\underline{H}_4 \xrightarrow[Q_1=[10.97]]{\Delta\nu = -98.7 cm^{-1}} Me_3C\underline{H} \qquad (1)$$

$\nu C\underline{H}$ 2992 cm^{-1} [10] 2893.3 cm^{-1} [10]

$\Delta\nu/1$ kcal mol^{-1}	Q_1 (kcal mol^{-1})	$\Delta H_f^0(Me_3C\cdot)$ (kcal mol^{-1})
14 cm^{-1}	7.05	13.76
12	8.22	12.59
11	8.97	11.84
10	9.87	10.94
9	10.97	9.84
8	12.34	8.47
6	16.45	4.36

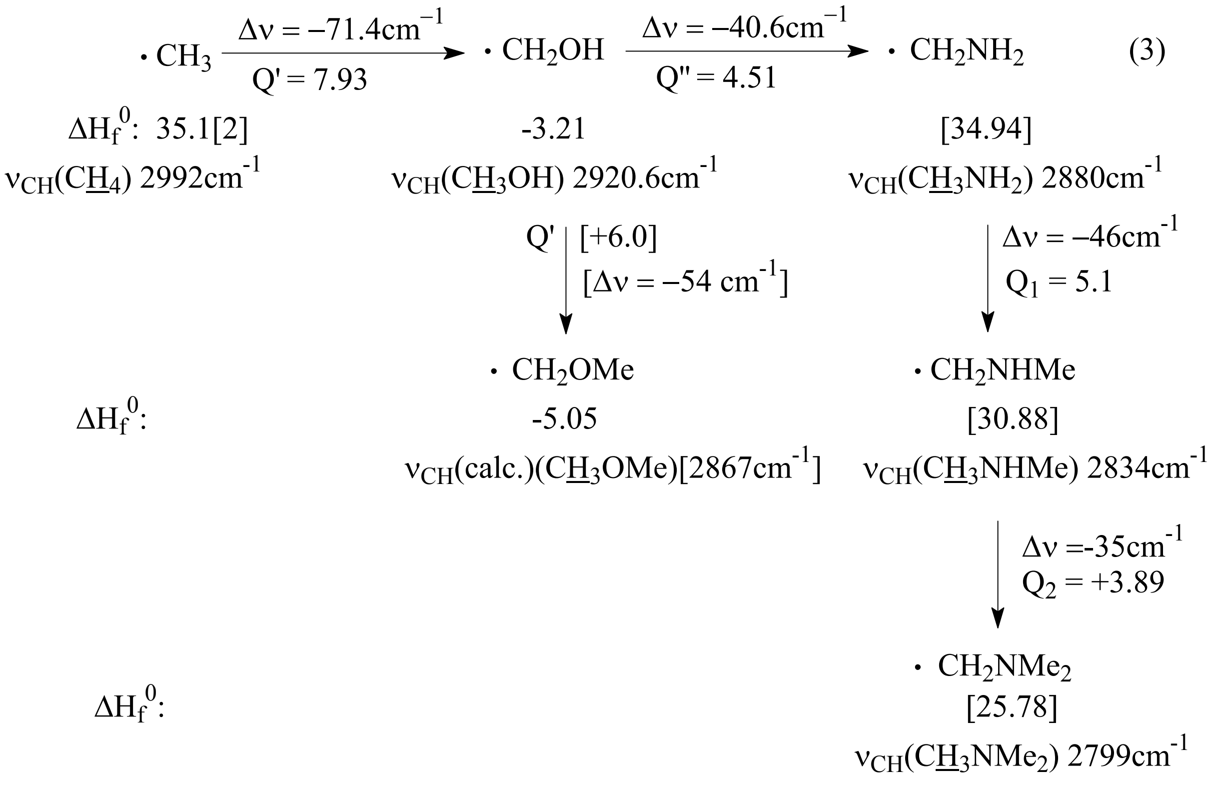
$$C\underline{H}_4 \xrightarrow[Q_2=[7.93]]{\Delta\nu = -71.4 cm^{-1}} C\underline{H}_3OH \qquad (2)$$

$\nu_{C\underline{H}}$ 2992 cm^{-1} [10] 2920.6 cm^{-1} [10]

$\Delta\nu/1$ kcal mol^{-1}	Q_2 (kcal mol^{-1})	$\Delta H_f^0(\cdot CH_2OH)$ (kcal mol^{-1})
11cm^{-1}	6.49	-1.77
10	7.14	-2.42
9	7.93	-3.21
8	8.93	-4.21
7	10.20	-5.48

To find out the Δν value corresponding to 1 kcal mol^{-1} in ΔBDE for aliphatic C–H bond we take two key examples, see Eqs. (1) and (2). In both equations we take a set of diverse random Δν values corresponding to 1 kcal mol^{-1} in ΔBDE. Then dividing the experimental Δν (–98.7 cm^{-1}) by each of these values we obtain diverse Q_1 (or Q_2) values and then applying the full form of isodesmic reaction we gain diverse ΔH_f^o values of Me_3C•, Eq. (1), or •CH_2OH, Eq. (2), radicals. For ΔH_f^o Me_3C• radical the range of quoted values is 4.5–14.3 kcal mol–1 ([2] and references therein). Computation gives higher values compared with experimental ones, *e.g.* 13.5 [14] or 14.3 [15] kcal mol^{-1}. In reference [2] the detailed analysis of the thermochemistry of alkyl radicals was performed using series of isodesmic reactions and finally the ΔH_f^0 value ~ 9.9 kcal mol^{-1} for Me_3C• radical was insistently advocated. This value corresponds to Δν 9 cm^{-1}/1 kcal mol^{-1}, Eq. (1), being also close to the mean value of the quoted values. Q_1 value is the heat of isodesmic reaction CH_3• + $Me_3CH \rightarrow CH_4$ + Me_3C• + Q_1 (full form) or CH_3• → Me_3C• + Q_1, Eq. (1) (brief form). For •CH_2OH radical the following values gained from chemical kinetics and photoionization studies are known: –6.2 [16], –5.1 [17], –4.08 [18], –3.5 [19], –2.9 [20], –2.5 [19], –2.15 [21] kcal mol^{-1}. Thus, we see that Δν (9 cm^{-1}) leads to ΔH_f^0 Me_3C• and •CH_2OH 9.84 and –3.21 kcal mol^{-1}, respectively, which are self–consistent and are close to the mean values quoted in the literature.

Now we come to Eq. (3) (ν_{CH} values – [6,10,12]; ΔH_f^o and Q values – in kcal mol^{-1}, the derived values – in square brackets; the isodesmic reactions are given in brief forms, *e.g.* •CH_3 → •CH_2OH + Q instead of •CH_3 + $CH_3OH \rightarrow CH_4$ + •CH_2OH + Q; the ΔH_f^0 values for molecules used in isodesmic reactions are taken from [22]):



Q values originate from full forms of isodesmic reactions, *e.g.* from brief form of $\bullet CH_3 \rightarrow \bullet CH_2OH + Q'$ isodesmic reaction we have $Q = \Delta H_f^o(CH_3\bullet) + \Delta H_f^o(CH_3OH) - \Delta H_f^o(\bullet CH_2OH)$ $\Delta H_f^o(CH_4) = 35.1 - 48.16 - (-3.21) - (-17.78) = 7.93$ kcal mol^{-1}, Eq. (3).

Since $\bullet CH_2OH$ radical is by ~ 4.5 kcal mol^{-1} (Q'') *less* stable than $\bullet CH_2NH_2$ free radical it is expected that in $\bullet CH_2OH \rightarrow \bullet CH_2OMe$ isodesmic reaction $Q' > Q_1$ since the less stable $\bullet CH_2OH$ radical might extract higher stabilization effect from the same (here, Me) group, (see Refs. [2–4] and compare Q_2 and Q_1 values in Eq. (3)). Taking an arbitrary Q' value ~ 6 kcal mol^{-1} (Q' and Q_1 would not differ much since Q'' value, *i.e.* difference in thermodynamic stabilities of $\bullet CH_2OH$ and $\bullet CH_2NH_2$ radicals is also not large) we get ΔH_f^o ($\bullet CH_2OMe$) = $-\Delta H_f^o$ ($\bullet CH_2OH$) – ΔH_f^o (CH_3OH) + ΔH_f^o (CH_3OCH_3) – Q' = –3.21 – (–48.16) – 44.0 – 6.0 = –5.05 kcal mol^{-1} and ν_{CH} ($C\underline{H}_3OMe$) = ν_{CH} ($C\underline{H}_3OH$) – Q' × 9 cm^{-1} = 2920.6 – 6 × 9 = 2866.6 cm^{-1}. This band is not fixed in IR spectrum but rather at 2883.4 cm^{-1} [6]. This being applied in Eq. (3) gives Q' 4.18 kcal mol^{-1} which does not fit the accurate and self–consistent data on ν_{CH} values for methylated amines. In Raman spectrum of gaseous CH_3OCH_3 molecule there is a band at 2868 cm^{-1} [23] which might correspond to IR ν_{CH} (calc.) 2866.6 cm^{-1}. Another candidate for the low lying band comes from IR spectrum of liquid CH_3OCH_3 molecule exhibiting strong band at 2845 cm^{-1} [24]. The corresponding band for gaseous molecule is expected to occur at slightly higher frequency 2850–2855 cm^{-1} (when solvent effect is taken in consideration) and hence ΔH_f^o ($CH_3OCH_2\bullet$) radical fits the data of Eq. (3). The experimental data for ΔH_f^o ($CH_3OCH_2\bullet$) are –2.8±1.2 [16], –5.0 [25] or –6.9 [26] kcal mol^{-1}.

The ΔH_f^o values of aminomethyl radicals, Eq. (3), 34.9, 30.9 and 25.8 gained from IR spectra although are close to literature values 35.7±2, 30.1±2 and 26.1±2 kcal mol^{-1} for $\bullet CH_2NH_2$, $\bullet CH_2NHMe$ and $\bullet CH_2NMe_2$ radicals, respectively (thus once more supporting the reliability of our $\Delta\nu$ 9 cm^{-1} per 1 kcal in ΔBDE), but are more accurate and self–consistent [16]. Earlier, it was found that for both ions (cations and radical–cations) and free radicals the consecutive H → Me substitution gave Q_2/Q_1 0.55±0.05 when this takes place at α–position to unsaturated carbon and Q_2/Q_1 ~ 0.75±0.05 when H → Me replacement occurs in β–position to cationic or radical–cationic centers. From Eq. (3) we gain Q_2/Q_1 0.75 for aminomethyl radicals whereas Q_2/Q_1 is 0.42 if we use the data gained from kinetics [16].

Taking the accurate values for ΔH_f^0 $HC(\bullet)=O$ 10.1 [27] and $\bullet COOCH_3$ –40.4 [16] kcal mol^{-1} and $\Delta\nu$ ($C\underline{H}_2=O \rightarrow \underline{H}COOMe$ = 117 cm^{-1} [6] we obtain Q –8.5 kcal mol^{-1} for $HC(\bullet)=O + HCOOCH_3 \rightarrow H_2C=O + \bullet COOMe + Q$ isodesmic reactions and 117 : 8.47 = 13.81 ~ 14 cm^{-1} for 1 kcal mol^{-1}. From this and the value 9 cm^{-1} for C–H bond in substituted alkanes (see above) it is clear that $\Delta\nu_{CH}$/1 kcal mol^{-1} value depends on the electronegativity (EN) of C–atom. There are no accurate experimental data for even two $CH_2=C(\bullet)H$ and $CH_2=C(\bullet)R$ (or $RCH=CH\bullet$) or $HC\equiv C\bullet$ and any $RC\equiv C\bullet$ free radicals. Therefore, by taking $\Delta\nu_{CH}$/BDE 9 cm^{-1} for alkanes, 14 cm^{-1} for $R\underline{C}H=O$ molecules and EN values 4.5–4.8; 5.3, 5.8 and 7.4 units for alkyl, $CH_2=CH$, $HC\equiv C$ and CHO groups (from Ref. [1]) we assign approximately $\Delta\nu_{CH}$ 11 and 12 cm^{-1} equivalent to 1 kcal mol^{-1} in ΔBDE (C–H) in alkenes and acetylenes, respectively. This finding allows to apply the data on gas phase IR spectra for description of the free radicals' heats of formation more accurately than it was done before when a unique value ~ 11 cm^{-1} was used for any type of C–H bond.

Now we come to calculation of the heats of formation for substituted ethynyl RC≡C• free radicals from IR spectra of RC≡C–H molecules. But to perform this we have to select the correct ΔH_f° value for unsubstituted ethynyl HC≡C• radical for which the experimental values (originating from pyrolysis and bimolecular chemical kinetics, diverse spectroscopic methods, ionization and appearance potential measurements) range from 110 to 139 kcal mol^{-1} while numerous *ab initio* and semi–empirical methods (including wide variation of model systems) give hundreds of values ranging from 87 to 163 kcal mol^{-1} [1]. Our computation results using PM3, AM1, MNDO, three *ab initio* methods and 21 isodesmic reactions gave 126 values in the range 50.6–177.3 kcal mol^{-1}. A disappointing result! The photofragmentation of acetylene molecule appeared to be a very complex process depending on method of investigation. From analysis of 17 experimental works on spectroscopy, photodissociation, photoionization, pyrolysis of acetylene we arrived to the decision to ascribe ΔH_f° HC≡C• 123±2 kcal mol^{-1} [1]. The details of the arguments in favor of this value are given in [1]. Here we give a single one. Let us consider the isodesmic reaction, Eq. (4), with ΔH_f° and Q in kcal mol^{-1}.

$$\cdot C{\equiv}N + HC{\equiv}CH \longrightarrow HC{\equiv}N + HC{\equiv}C\cdot + Q \qquad (4)$$

	$\cdot C{\equiv}N$	$HC{\equiv}CH$	$HC{\equiv}N$	$HC{\equiv}C\cdot$	Q
ΔH_f^0	104	54.5	32.6	135 [28]	-9.1
				131 [29, 30]	-5.1
				[125.9]	0
				123*±2	+2.9*
				122 [31]	+3.9
				120.5 [32]	+5.4

*) this work

ΔH_f^0 •C≡N 104.1±0.5 was determined experimentally by three methods [33]. The higher value is quoted 105.5 kcal mol^{-1} [34]. Tsang "insisted" on much lower value 99 kcal mol^{-1} [35]. There is also a novel experimental value for HCN molecule 30.8 kcal mol^{-1} [36]. From the well documented properties of HC≡C– and N≡C– groups [1,22,28,31,37,38] the latter is a stronger electron–withdrawing group than the former thus making Q > 0 in Eq. (4). Since it is not possible to evaluate the Q value in Eq. (4), for a moment we accept the value 123 kcal mol^{-1} for ΔH_f° HC≡C• radical as the most reliable. If ΔH_f° •C≡N 99 kcal mol^{-1} is accepted then ΔH_f° HC≡C• will further go down [35].

The experimental data on ΔH_f° values of substituted ethynyl RC≡C• radicals are not available whereas there is a wealth of ν (RC≡C–H) values in gas phase IR spectra. Using these data (for literature sources see [1]), the ΔH_f° values for parent molecules RC≡CH which are also calculated using enthalpic shift procedure and $\Delta\nu_{CH}/\Delta BDE$ 12 cm^{-1} equivalent for 1 kcal mol^{-1} we calculated the heats of formation for many RC≡C• free radicals (SE – stabilization energy, ΔH_f° values and SE in kcal mol^{-1}, all literature sources are given in [1]).

Table. Thermochemical data on RC≡C• free radicals and there parent RC≡CH molecules

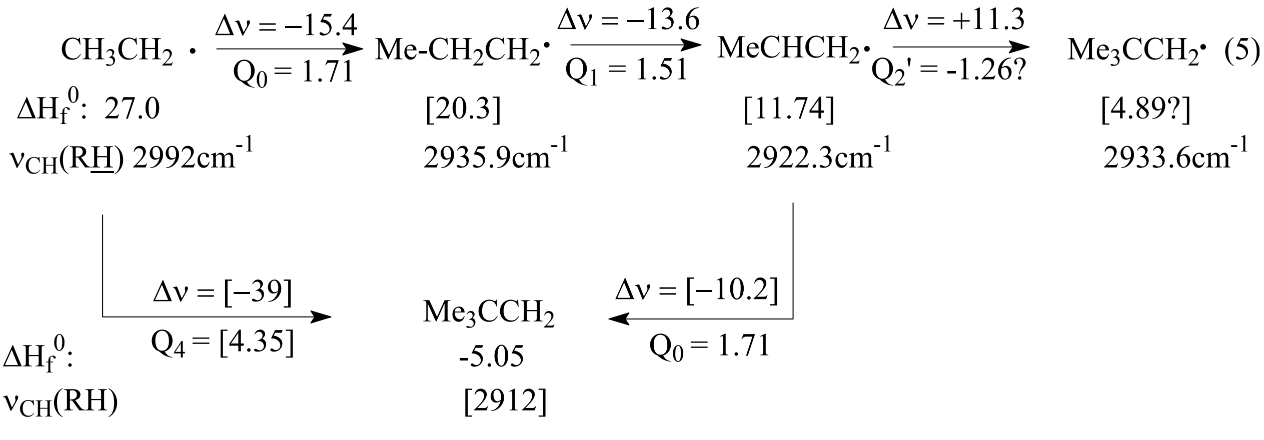
RC≡C•	ν(RC≡CH) cm^{-1}	Δν(HC≡CH → RC≡C$\underline{H}$) cm^{-1}	SE (HC≡C• → RC≡C•)	ΔH_f^0 (RC≡C•)		ΔH_f^0(RC≡CH) [1]
				this work	lit.	
HC≡C•	3335.6	0.0	0.0	123	see text	54.54 [22]
CH_3C≡C•	3334.49	–1.11	–0.09	111.56	107.5, 109, 116.3, 123.8, 125.1, 128.6, 143.9	44.2 [22]
C_2H_5C≡C•	3332	–3.6	–0.3	106.66	101.7	39.5 [22]
Me_3CC≡C•	3329.37	–6.23	–0.52	92.51		25.57
HC≡CC≡C•	3332.15	–3.45	–0.29	180.17	165.5, 170.7, 186.4, 188.6, 197.5, 201	113
PhC≡C•	3328	–7.6	–0.63	145.13	153.4, 156.3, 158.2	78.4
FC≡C•	3357.0	21.36	1.78	75.24	75.5, 83±20, 105.8, 107.8, 108.5, 109.1	6.0
ClC≡C•	3340.7	5.1	0.43	113.4	114.5, 135.7	45.5
CF_3C≡C•	3327.3	–8.3	–0.7	–44.24	–25.9	–111
N≡CC≡C•	3327.4	–8.2	–0.69	153	131, 145.6, 149, 150, 158, 169.7, 178.2	86.2
CNC≡C•	3339	3.4	0.28	174.24		106.5
F_5SC≡C•	3327.55	–8.05	–0.68	106.86		–175
Me_3SiC≡C•	3312.46	–23.14	–1.93	69.53		4

It is remarkable that most of the substituents stabilize ethynyl radical compared with unsubstituted one. This can be explained by low thermodynamic stability of HC≡C• radical which extracts stabilization even from such traditionally electron–withdrawing groups as CF_3, NC– or SF_5. Their polarizability effects, which are opposite to their EN effects, come in action [1]. This is supported by the fact that only small (F, Cl, HO) or charged ($^{-}C≡N^{+}$–) substituents destabilize the HC≡C• free radical.

3 NEGATIVE RESULTS AND DIFFICULTIES

Among 25 substituted methanes CH_3X (F, Cl, Br, I, CF_3, CH_2Cl, $CHCl_2$, CCl_3, SH, PH_2, NO_2, ONO_2, CN, C_2H_3, Ph, C≡CH), CH_2X_2 and CHX_3 (X = F, Cl, Br, I) only in case of $C\underline{H}F_3$, $C\underline{H}_3CH_2Cl$, $C\underline{H}_3CHCl_2$, $C\underline{H}_3CCl_3$ and $C\underline{H}_3CF_3$ $\Delta\nu_{C\underline{H}}$ (exp.) (from [1,6–12] are in consensus with BDE C–H bonds gained from the known ΔH_f° values of R• free radicals. In all other cases $\nu_{C\underline{H}}$ (exp.) exceeds ν_{CH} value expected from ΔH_f° (R•) (lit.) (when taking $\Delta\nu/\Delta BDE$ 9 cm^{-1}/1 kcal mol^{-1}) by 25–189 cm^{-1} or 2.8–21 kcal mol^{-1} in ΔBDE. For some of such molecules ($PhC\underline{H}_3$, CH_2=$CHC\underline{H}_3$, $C\underline{H}_3F$, $C\underline{H}_2F_2$) the explanation of deviation to higher ν_{CH} values is straightforward: the loss in IR spectrum of the band for C–H bond which trans– to either heteroatom's lone pair (O, N) or to π–system. Such lost band with lowest ν_{CH} belongs to the conformer with lowest BDE, i.e. the less thermodynamically stable conformer in relation to dissociation process. But for the most of the other CH_3X, CH_2X_2 and CHX_3 molecules giving large deviations to higher frequencies one should address, probably, to involvement of "excited" states analogous to those in UV– or electron impact ionization.

When such "excitation" is large it is hardly possible to ascribe the observed ν_{CH} value to the process of formation of R• radical in its ground state. However, when such increase in ν_{CH} value is a small one this value can be treated as responsible for "adiabatic" dissociation leading to calculation of the "true" R• heat of formation. Therefore, all data in ν_{CH} values might be verified using isodesmic reactions like it was done above with CH_3OCH_3 molecule, Eq. (3). Here we give one more example, Eq. (5), (ν_{CH} values – [10]; ν and Δν in cm^{-1}; ΔH_f^o and Q – in kcal mol^{-1}; Δν 9 cm^{-1} is taken for equivalent of 1 kcal mol^{-1}; derived values – in square brackets)



We observe the well–known attenuation effect with $Q_1 < Q_2$ (both values >0) at successive introduction of electron–releasing Me–group to yet more stable free radical (compare with Eq. (3) and see references [1,2,4,5]). Therefore, the rise of ν_{CH} value from $Me_2CHC\underline{H}_3$ to $Me_3CC\underline{H}_3$ by 11.3 cm^{-1} which might indicate destabilization of free radical at H → Me replacement seems strange. Really, such replacement decreases ν_{CH}, Eqs, (3), (5) and Table). Taking $Q_2/Q_1 \sim 0.75$ for β–substitution (see above) we obtain Q_2 $1.51 \times 0.75 = 1.13$ kcal mol^{-1} and Δν (calc.) –10.2 cm^{-1} for $Me_2CHC\underline{H}_3 \rightarrow Me_3CC\underline{H}_3$ which gives ν_{CH}(calc.) in $Me_3CC\underline{H}_3$ 2922 – 10.2 ~ 2912 cm^{-1}. Such band is absent for unknown reasons in IR spectrum of neopentane Me_4C but in Raman spectrum of gaseous and liquid of this substance there are the bands at 2923 and 2912 cm^{-1}, respectively [39]. Thus, we gave several examples when the band "missing" in gas–phase IR spectra can be found in Raman spectra of either gaseous or liquid substances. Now we again verify the $\Delta\nu_{CH}$(calc.) for $Me_3CC\underline{H}_3$ 2912 cm^{-1} leading to ΔH_f^o Me_3CCH_2• 2.5 kcal mol^{-1}, Eq. (5) by the isodesmic reaction $Me–CH_2$• + Me_4C → C_2H_6 + Me_3CCH_2• + Q or brief form: $MeCH_2$• → Me_3CCH_2• + Q, Eq. (6), suggesting diverse literature values for the heat of formation for $Me_3CCH_2\bullet$ free radical (ΔH_f^o and Q – in kcal mol^{-1}).

$$\mathrm{Me\text{-}CH_2\bullet} \rightarrow \mathrm{Me_3C\text{-}CH_2\bullet} + \mathrm{Q} \qquad (6)$$

	Me-CH$_2$•	Me$_3$C-CH$_2$•	Q
ΔH_f^0:	27.0	2.5*	+ 4.35
		4.6 [17]	+ 2.25
		4.89**	+1.96
		5.57	+1.35
		6.7 [40]	+0.15
		8.7 [34]	–1.85
		10.0 [41]	–3.15

* suggested in this work
** calculated from ν_{CH}(exp.) in Me_3CCH_3

The value 2.5 kcal mol^{-1} seems to be most reliable since Q 4.35 kcal mol^{-1} corresponding to the three H → Me replacements in β–position stands in line with Q' 6.44 kcal mol^{-1} for $MeCH_2\bullet \rightarrow Me_3C\bullet$ reaction with two H → Me replacements in α–position (Q' comes out of ν_{CH} 2951.3 and 2893.3 cm^{-1} in $MeC\underline{H}_3$ and $Me_3C\underline{H}$ molecules [10], respectively). The small positive, or, even more, negative Q values in Eq. (6) are in obvious conflict with known electron–releasing properties of Me–group.

Now we briefly mention other possible sources of errors and difficulties in application of gas phase IR spectra to thermochemistry of free radicals. The first one is the problem of correct ascribing of the experimental band to namely C–H vibration. The second one is the expected difference between the ν_{CH} of undeuterated and deuterated molecules when ν_{CH}(isolated) frequencies are measured in $–CHD_2$ and –CHD–groups. In this work we claim the importance of EN of carbon atom for the value $\Delta\nu_{CH}$ in, say, CH_2X and CHX_2 groups depending on the EN of X–atom or group. But, we adjust the single value 9 cm^{-1}/1 kcal mol^{-1} to all saturated aliphatic compounds.

Nevertheless, we think that we demonstrated the utility of IR spectra for the thermochemistry of free radicals when they are combined with isodesmic reaction control.

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5 REFERENCES

[1] A. V. Golovin, V. V. Takhistov, Thermochemistry of organic and heteroorganic species. Part XII. Mono– and disubstituted acetylenes and ethynyl free radicals. *J. Mol. Struct.*, in press
[2] D. A. Ponomarev, V. V. Takhistov, Some regularities in thermodynamic stability of free radicals, *J. Mol. Struct.*

1997, *435*, 259–274.

[3] D. A. Ponomarev, V. V. Takhistov, The enthalpies of formation of the hydrides of main group elements, *J. Mol. Struct.* **1999**, *477*, 91–103.

[4] Yu. D. Orlov, G. Bouchoux, V. V. Takhistov, D. A. Ponomarev, A new estimation scheme of the enthalpies of formation for RCH_2• free radicals, *J. Mol. Struct.* **2001**, *608*, 109–122.

[5] D. Ponomarev, V. Takhistov, Isodesmic Reactions and Thermochemistry of Free Radicals, *Abstracts of 5th International Conference on Chemical Kinetics*, *Gaithersburg*, *USA*, *July 16–20*, *2001*, 61–62.

[6] D. C. McKean, Individual CH bond strength in simple organic compounds, *Chem. Soc. Rev.* **1978**, *7*, 399–422.

[7] D. C. McKean, B. W.Laurie, Isolated CH stretching frequencies, bond lengths and strengths in chloroalkanes, *J. Mol. Struct.* **1975**, *27*, 317–328.

[8] D. C. McKean, S. Biedermann, H. Burger, CH bond lengths and strengths, unperturbed CH stretching frequencies, from partial deuteration infrared studies: t–butyl compounds and propane, *Spectrochim. Acta* **1974**, *30A*, 845–857.

[9] D. C. McKean, CH stretching frequencies, bond lengths and strengths in halogenated ethylenes, *Spectrochim. Acta* **1975**, *31A*, 1167–1186.

[10] J. L. Duncan, D. C. McKean, I. Torto, A. Brown, A. M. Ferguson, Infrared studies of methylidyne and methylidyne–d stretching anharmonicity, *J. Chem. Soc. Faraday Trans. 2.* **1988**, *84*, 1423–1442.

[11] B. J. Van der Veken, R. O. Oderus, A. Brown, D. C. McKean, A. R. Morrison, Gas phase infrared contour simulation of isolated C–H stretches in butane–d_9, *J. Mol. Struct.* **1986**, *147*, 57–65.

[12] D. C. McKean, CH bond dissociation energies, isolated stretching frequencies, and radical stabilization energy, *Int. J. Chem. Kinet.* **1989**, *21*, 445–464.

[13] D. C. McKean, Quantum–chemical studies of fluoroethanes: vibrational assignments, isolated CH stretching frequencies, valence force constants, and bond lengths relationships, *J. Phys. Chem.* **2000**, *A104*, 8995–9008.

[14] D. J. Henry, M. B. Sullivan, L. Radom. G3–RAD: Modified Gaussian 3(G3) and Gaussian–3X (G3X) procedures for radical thermochemistry, *J. Chem. Phys.* **2003**, *118*, 4849–48460.

[15] L.A.Curtiss, K.Ragavachari, P.C.Redfern, J.A.Pople, Assessment of Gaussian–2 and density functional theories for the computation of enthalpies of formation, *J.Chem.Phys.* **1997**, *106*, 1063–1079.

[16] D.F.McMillen, D.M.Golden, Hydrocarbon bond dissociation energies, *Ann.Rev.Phys.Chem.* **1982**, *33*, 493–532.

[17] Yu.D.Orlov, Yu.A.Lebedev, I.Sh.Saifullin. *Thermochemistry of Organic Free Radicals* (*Russ.*), Nauka, Moscow, 2001.

[18] Y.–R.Luo. *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press, Boca Raton, 2003.

[19] S.Dobe. On the enthalpy of formation of hydroxymethyl, *Zeitschr.Physikal.Chem.* **1992**, *175*, 123–124.

[20] J.Berkowitz, G.B.Ellison, D.Gutman, Three methods to measure RH bond dissociation energies, *J.Phys Chem.* **1994**, *98*, 2744–2765.

[21] S.Dobe, M.Otting, F.Temps, H.Gg. Wagner, H.Ziemer, Fast flow kinetic studies of the reaction $CH_2OH + HCl \leftrightarrow CH_3OH + Cl$. The heat of formation of hydroxymethyl, *Int.J.Phys.Chem*, **1993**, *97*, 877–883.

[22] J.B.Pedley, R.D.Naylor, S.P.Kirby. *Thermochemical Data of Organic Compounds*, *2nd ed.*, Chapman and Hall, New York, 1986.

[23] R.C.Taylor, G.L.Vidale, Raman spectrum and vibrational assignment of gaseous dimethyl ether, *J.Chem.Phys.* **1957**, *26*, 122–123.

[24] Y.–i.Mashiko, K.S.Pitzer, Vibrational spectra of dimethyl ether in the lower frequency region, *J.Phys.Chem.* **1958**, *62*, 367–368.

[25] L. F. Loucks, K. J. Laidler, Thermochemistry of the methoxymethyl radical, *Can. J. Chem.* **1967**, *45*, 2786–2792.

[26] D. M. Golden, S. W. Benson, Free–radical and molecule thermochemistry from studies of gas–phase iodine–atom reactions, *Chem. Rev.* **1969**, *69*, 124–134.

[27] A. C.Terentis, S. H. Kable, Near threshold dynamics and dissociation energy of the reaction $H_2CO \rightarrow HCO + H$, *Chem. Phys. Lett.* **1996**, *258*, 626–632.

[28] S. G. Lias, G. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, J. Mallard. Gas–phase ion and neutral thermochemistry, *J. Phys. Chem. Ref. Data.* **1988**, *17*, *Suppl 1.*

[29] J. Segall, R. Lavi, Y. Wen, C. Wittig, Acetylene C–H bond dissociation energy using 193.3 nm photolysis and sub–doppler resolution H–atom spectroscopy: 127±1.5 kcal mol^{-1}, *J. Phys. Chem.* **1989**, *93*, 7287–7289.

[30] P. G. Green, J. L. Kinsey, P. W. Field, A new determination of the dissociation energy of acetylene, *J. Chem. Phys.* **1989**, *91*, 5160–5163.

[31] S. W. Benson, *Thermochemical Kinetics*, J.Wiley, New York, 1976.

[32] Yu. P. Jampolskii, V. V. Zelentsov, Heat of formation of ethynyl radical, *React. Kinet. Catal. Lett.* **1981**, *17*, 347–353.

[33] Y. Huang, S. A. Barts, J. B. Helpern, Heat of formation of the CN radical, *J. Phys. Chem.* **1992**, *96*, 425–428.

[34] D. R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, *CRC Press*, *Boca Raton*, *77th ed*, **1996–1997**, 1997.

[35] W. Tsang, Chemical kinetic data base for propellant combustion. II. Reactions involving CN, CNO and HCNO, *J. Phys. Chem. Ref. Data* **1984**, *13*, 753–792

[36] E. P. Clifford, P. G. Wenthold, W. C. Lineberger, G. A. Peterson, K. M. Broadus, S. R. Kass, S. Kato, C. H. DePuy, V. M. Bierbaum, G. B. Ellison, Properties of diazocarbenes [CNN] and diazomethyl radical [HCNN] via ion chemistry and spectroscopy, *J. Phys. Chem.* **1998**, *102*, 7100–7112.
[37] A. N. Vereshaguin, *Inductive Effect. Substituent Constants for Correlation analysis* (*Russ*), Nauka, Moscow, **1988**.
[38] C. Hansch, A. Leo, R. W. Taft, A survey of Hammet substituent constants and resonance and field parameters, *Chem. Rev.* **1991**, *91*, 165–195.
[39] A. H. S. Matterson, L. A. Woodward, Relative intensities of totally symmetrical vibrations in the Raman spectrum of gaseous neopentane, *Proc. Roy. Soc. A*. **1955**, *231*, 514–516.
[40] M. Frenkel, K. N. Marsh, R. C. Wilhoit, G. S. Kabo, G. N. Roganov, *Thermodynamics of Organic Compounds in the Gas Phase*. Thermodynamics Research Center, College St., TX, USA, **1994**.
[41] J. Espinosa–Garcia, J. C. Garcia–Bernaldez, Theoretical Enthalpies of formation of large compounds using integrated method, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4096–4102.

Biographies

Aleksander Golovin was born in 1951. From 1969 up to now he was a student, post graduate and then working as a researcher in a staff of the Department of Photonics in the Faculty of Physics of St. Petersburg University (Russia). He is a highly qualified specialist in photoionization and applied mass spectrometry. In this area he worked in laboratories of France, Germany, Britain, USA (Ford Motor Co) and Japan.

Dmitry Ponomarev was born in 1946. He graduated from the Faculty of Chemistry of St. Petersburg University (Russia) in 1969 and began working in St. Petersburg Forest Technical Academy, first as an Assistant Professor, than as an Associate Professor and since 1997 as a Professor in the Department of Organic Chemistry. In 1974 he submitted a thesis entitled “Influence of alkyl substituents on the stability of cations in the absence of solvent” and was awarded a PhD from St. Petersburg University. D. A. Ponomarev received the degree of Doctor of Science in 1997 at St. Petersburg Forest Technical Academy, having represented a thesis “Thermochemistry of lignin model compounds and its intermediates in the reactions of homolytic destruction”. D. A. Ponomarev is an author of several review papers and of over 80 original publications. In 1977–78 he worked for a year in the laboratory of Prof. G. Brunow at University of Helsinki, in 1998 for a month as a visiting scientist in the laboratory of Prof. P. Vainiotalo at University of Joensuu, Finland, and in 2001 for a six months in the laboratory of Dr. T. Wallington (Ford Motor Co), Dearborn, USA.

Viatcheslav Takhistov was born in Leningrad (Russia) in 1938. From 1955 up to 1997 he was student, post graduate, assistant professor, docent in the Faculty of Chemistry of Leningrad (St. Petersburg) University (Departments of Physical Organic Chemistry and Chemistry of Natural Products). From 1997 up to now he is a senior researcher in Academic Research Institute “Center of Ecological Safety” (St. Petersburg). His PhD (1967) and Dr. Sci (1989) dissertations are dedicated to thermochemical description of fragmentation rules for positively and negatively charged ions in mass spectrometer. He is an author of more than 80 publications (essential part with D. Ponomarev), including two books in organic mass spectrometry, thermochemistry of ions and free radicals, structural elucidation of novel potential ecotoxicants in waters of North–West Russia and Finland. On long–time terms he worked in laboratories of Scotland, Germany, Finland and USA (Ford Motor Co, Dearborn).