Ab initio calculations of the vibronically averaged hyperfine coupling constants for the 1 $^2\Pi_u$ electronic state of CH$_2^+$

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The results of pure *ab initio* calculations of the hyperfine coupling constants for the 1 $^2\Pi_u$ electronic state for various isotopomers of CH$_2^+$ in the energy range between 0 and 20 000 cm^{-1} are presented. Effects of vibronic and spin–orbit coupling are discussed.

I. INTRODUCTION

With the present study we continue our *ab initio* investigation of the hyperfine structure of spectra of small polyatomic molecules characterized by two of more electronic states strongly interacting with each other.[1-4] In the previous papers it has been shown that a reliable reproduction of the values for the hyperfine coupling constants (hfcc's) derived by experiment can be achieved only if proper averaging of the corresponding *ab initio* calculated quantities over the vibronic states in question is performed. As stated in these studies the variation of the vibronically averaged hfcc's (in the following text we shall use the term "vibronic hfcc's" for these quantities and "electronic hfcc's" for the electronic matrix elements of the hfcc's) from one vibronic level to another reflects generally three effects, connected more or less with each other: (i) geometry dependence of the electronic matrix elements of the hfcc's; (ii) composition of the vibronic wave functions, particularly the amount of the various coupled electronic states in them; (iii) strong local coupling between (accidentally) close-lying vibronic levels belonging in the zeroth-order approximation to different electronic states. In the electronic species split as a consequence of the Renner–Teller effect[5] the vibronic coupling affects most largely (systematically) the mean values for the hfcc's of the levels in the energy region around the point where both component states touch one another at the linear molecular geometry.[3,4] For the levels far from that it has significant effect only in the case of above mentioned near degeneracies. However, it has been shown[2] that experimentally detectable effects can be expected even if the interacting electronic states are separated from one another by as much as some thousand wave numbers (for example, it has been found that the measured ratio between the isotropic hfcc for the light centers in the lowest vibronic levels of C$_2$H and C$_2$D deviates substantially from the ratio of the respective g_N values. That has been explained by the different magnitude of the vibronic mixing in these two species[2]). Thus, generally, only those hfcc's can be compared with experimental data which are calculated by taking into account the influence of both the electronic and nuclear motions.

Experimental determinations of the values for the hfcc's in various vibronic levels is a very expensive task. First, a lot of measurements are necessary and second, in order to extract the values for hfcc's, a knowledge of relevant molecular constants for each of the vibronic levels of interest is required. Furthermore, the current experimental techniques do not enable us to obtain all anisotropic hfcc's.[6] Finally, very often it is not possible to get insight into reasons for variation of the values for hfcc's from one vibronic level to another.

The above listed disadvantages disappear by theoretical determination of the hfcc's. All components of the hf tensor can be computed and a single solution of the nuclear Schrödinger equation gives the values for the vibronic hfcc's in all states of interest. Not only the magnitude of the differences between the values of the hfcc's for various vibronic states but also explanation of their origins is obtained. A serious drawback of theoretical investigations is generally their lower accuracy compared to experiment; however, recent studies[7,8] have shown that it is possible to overcome to a large extent the well-known difficulties by *ab initio* calculations of the electronic mean values for (isotropic) hfcc's[9] if a (configuration–interaction) CI/B_K (Ref. 10) treatment is applied.

While in the above mentioned studies[2-4] a direct comparison of the theoretical results with the experimental findings was possible for both the lowest-lying and some of the higher[3,4] vibronic levels, the results of the present work are of pure predictive nature because there has been practically no experimental information concerning the CH$_2^+$ spectrum thus far. An attempt to study the hyperfine structure of the ground vibronic level of this radical using the electron-spin resonance (ESR) technique failed because of the appearance of overlapping lines arising from several other species.[11] Only very recently detection of the infrared spectrum resulting in the determination of the ν_3 fundamental has been reported.[12] Several *ab initio* studies concerning the formation and dissociation of CH$_2^+$ and the vibronic structure of its lowest lying electronic states $X\,^2A_1$ and $A\,^2B_1$ correlating at the linear geometry to the 1 $^2\Pi_u$ species have been published.[13-25] An extensive pure *ab initio* investigation of the vibronic and fine structure of the coupled $X\,^2A_1$ and $A\,^2B_1$ states has recently been performed in our laboratory.[26] On the basis of the theoretical studies it follows that the ground electronic state $X\,^2A_1$ with the dominant configuration $(1a_1)^2\,(2a_1)^2\,(1b_2)^2$

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$(3a_1)^1$ has a slightly bent equilibrium geometry with a bond angle of about 140° and a barrier to linearity of roughly 1000 cm^{-1} (for a detailed comparison of various theoretical results the reader is referred to Ref. 26) representing in this way an excellent example of quasilinearity. The equilibrium geometry of the other 1 $^2\Pi_u$ component, A $^2B_1$, [dominant configuration $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(1b_1)^1$] is linear. Thus the CH$_2^+$ radical lies between the two systems mentioned above, C$_2$H, for which all three interacting species X $^2\Sigma^+(1 A')$ and A $^2\Pi(1$ $^2A''$, $2^2A')$ prefer linear equilibrium structure, and NH$_2$, where both the components of the 1 $^2\Pi_u$ species have bent equilibrium geometries. Interesting vibronic effects on the hyperfine structure of the CH$_2^+$ spectrum are expected already in the lowest vibronic states of this radical which is of considerable astrophysical importance.

FIG. 1. Effective bending potential curves for the X $^2A_1$ and A $^2B_1$ electronic states of CH$_2^+$. Calculated positions of $K=0$ (solid lines) and $K=1$ (dashed lines) vibronic levels are indicated and denoted by the quantum number v_2^{bent} (see text for explanation).

II. CALCULATION OF ELECTRONIC MEAN VALUES FOR THE hfcc's

The atomic orbital (AO) basis employed in the present study for the carbon atom consists of the $(13s8p)$ Gaussians in the $[8s5p]$ contraction, as proposed by van Duijnefeld;[27] it is augmented by three d functions with exponents $\alpha_d=2.292$, 0.838, and 0.292 (Ref. 28) for a better description of the polarization effects, as well as by two additional d species ($\alpha_d=8.0$, 0.1) which are known to improve the computation of the isotropic hfcc.[8,29] Finally a diffuse s ($\alpha_s=0.02$) and p ($\alpha_p=0.0358$) function are added to the carbon AO basis set. For the hydrogen atom the $(8s)$ set of van Duijnefeld[27] in a $[5s]$ contraction is augmented by two s functions ($\alpha_s=2.593$, 0.01) and three p functions ($\alpha_p=1.848$, 0.649, 0.228).[28]

All calculations are performed within the C_{2v} point group and the electronic hfcc's are computed employing the multiple reference double-excitation configuration–interaction (MRD-CI) method in connection with a modified B_K correction.[7] In contrast to the configuration–interaction (CI) treatment applied by calculation of the potential curves and the electronic transition moments[26] where the $1s$ orbital of the carbon atom is kept doubly occupied, in the present calculations all electrons are correlated and no virtual orbitals are discarded because it has been found that the correlation effects involving the inner shell electrons are very important for reliable calculation of the isotropic hfcc. An energy threshold of $T=0.1$ μH is used as the criterion for selecting the configurations within the MRD-CI procedure. In the framework of the B_K treatment all the coefficients in the CI expansion with a magnitude greater than 0.002 as well as the coefficients of the configurations generated by single excitations from the main reference species (total number of roughly 2000–3000) are corrected. The approximate natural orbitals of the electronic state in question are employed as the one-particle basis.
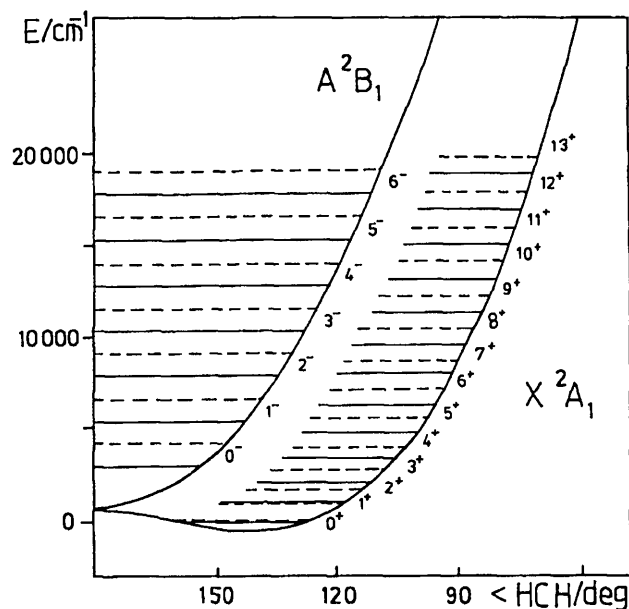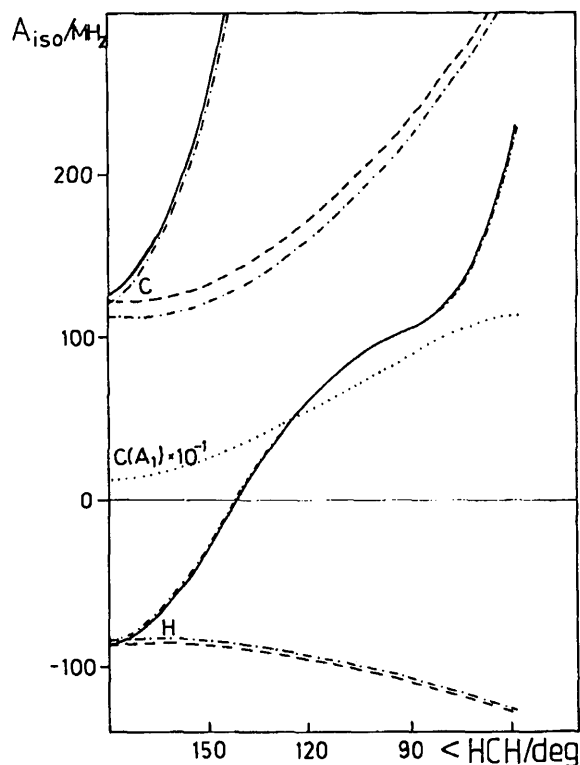

FIG. 2. Bond angle dependence of the electronic means values of the isotropic hfcc for the carbon and hydrogen atoms in the 1 $^2\Pi_u$ state of CH$_2^+$. Solid lines: X $^2A_1$ (electronic) state; dashed lines: A $^2B_1$ state. Dotted line represents the isotropic hfcc in the X $^2A_1$ state multiplied by the factor 0.1. Dashed–dotted lines: results obtained without B_K correction.
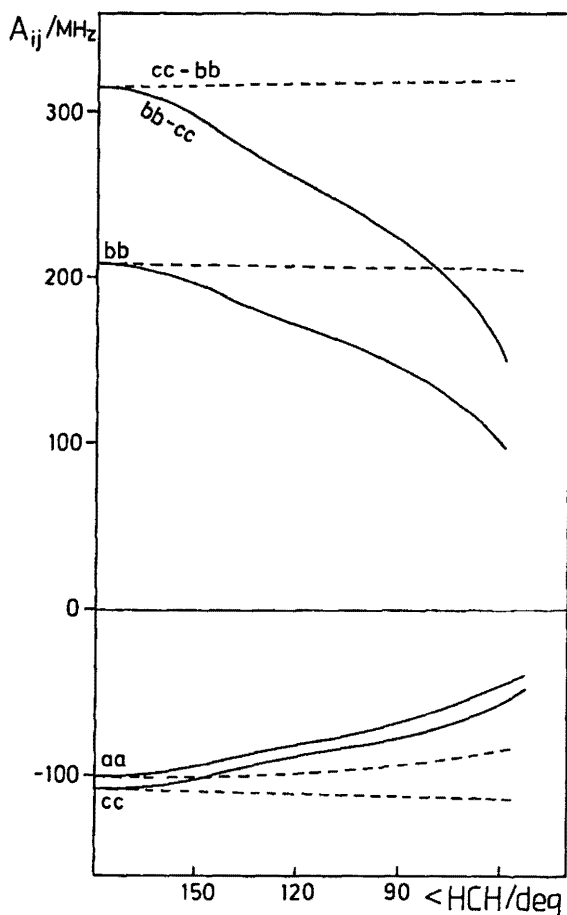
FIG. 3. Components of the anisotropic hf tensor for the carbon atom in the principal inertia axes system of CH$_2^+$. Solid lines: in the $X\,^2A_1$ electronic state; dashed lines: in the $A\,^2B_1$ state.
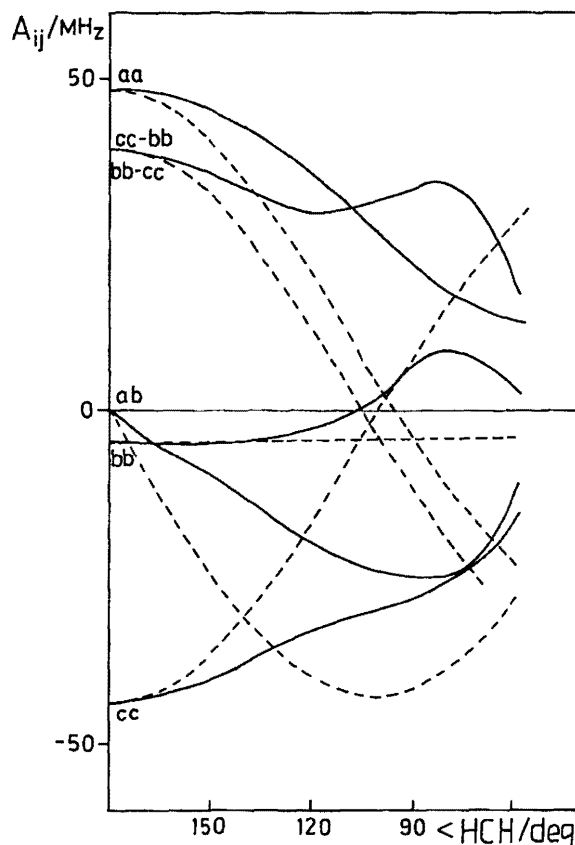
FIG. 4. Components of the electronic mean values of the anisotropic hf tensor for the hydrogen atom. Solid lines: in the $X\,^2A_1$; dashed lines: in the $A\,^2B_1$ state.

III. COMPUTATION OF VIBRONICALLY AVERAGED hfcc's

The approach employed for calculation of the vibronic hfcc's is described in detail in Ref. 4 and here we give only a brief summary. The Hamiltonian derived by Bunker and co-workers,[31,32] allowing for treatment of the large amplitude bending vibrations and incorporating (if necessary) the leading part of the bend–stretch interaction is adjusted to the problem of two electronic states coupled via the Renner–Teller effect.[33] It is assumed that the stretching vibrations, as well as the rotations around the axes orthogonal to the smallest moment of inertia axis a, can be separated. The projection of the total angular momentum (excluding spin) onto the axis a, coinciding at the linear nuclear arrangement with the molecular axis, is assumed to be conserved; the corresponding quantum number is denoted by K. These usual approximations[34] for CH$_2^+$ are even more justified than in the case of NH$_2$ because of the relatively weak dependence of the optimized C–H bond lengths on the bending coordinate,[26] and the corresponding weaker bend–stretch coupling, and the more pronounced quasilinearity of the 1 $^2\Pi_u$ electronic state of CH$_2^+$. The remaining degrees of freedom (electronic motion, bending,

and a-axis rotation) are treated simultaneously. The corresponding Schrödinger equation is solved variationally where the vibronic wave functions are represented by expansions in the eigenfunctions of a two-dimensional harmonic oscillator. The vibronic hfcc's are computed as integrals over the vibronic wave functions.

IV. RESULTS AND DISCUSSION

The effective bending potential curves (corresponding to optimized C–H bond lengths) employed in the present paper are shown in Fig. 1. They have practically the same shape as those published in Ref. 26. The use of a larger AO basis and the opening of the 1s core of the carbon atom in the present CI calculations of the electronic hfcc's has in consequence a parallel shifting of all energy points by $\simeq$ 0.040 hartree. The calculated $K=0$ and $K=1$ vibronic levels are also indicated in Fig. 1. They are labeled by the bending quantum number v_2 in the "bent" notation.[34] The relation between $v_2^{\rm bent}$ and another often used quantum number $v_2^{\rm lin}$ is given by $v_2^{\rm lin}=2\times v_2^{\rm bent}+\Lambda(=1)+K$. Note that only the lowest $K=0$ and $K=1$ vibronic levels ($v_2^{\rm bent}=0$) of the $X\,^2A_1$ electronic state lie below the barrier to linearity.

The dependence of the electronic isotropic hfcc and the Cartesian (in the principal axis of inertia system) as well as the irreducible tensor components of the anisotropic hf

TABLE I. Computed vibronic mean values for the isotropic hfcc and the aa component of the anisotropic hf tensor in the $K=0$ levels of the $1\,^2\Pi_u$ electronic states of CH_2^+. The vibronic levels are labeled by the bending quantum number v_2^{bent}, those belonging to the $A\,^2B_1$ state also by v_2^{lin} (in parentheses). The superscripts $+$ and $-$ correspond to the $X\,^2A_1$ and $A\,^2B_1$ component electronic states, respectively.

| | $^{12}CH_2^+$ | | | $^{13}CH_2^+$ | | | |
| | | H | | | ^{13}C | | H |
v_2 ($K=0$)	E (cm$_{-1}$)	A_{iso} (MHz)	A_{aa} (MHz)	E (cm^{-1})	A_{iso} (MHz)	A_{aa} (MHz)	A_{iso} (MHz)
0^+	0	−0.606	42.7	0	347	−90.8	−0.643
1^+	1 034	−5.16	42.4	1 028	346	−90.9	−5.30
2^+	2 175	1.14	41.4	2 161	373	−89.7	0.943
$0^-(1)$	3 058	−88.7	45.3	3 048	126	−99.9	−88.7
3^+	3 464	9.72	40.1	3 441	407	−88.2	9.50
4^+	4 881	17.3	39.0	4 849	440	−86.9	17.1
$1^-(3)$	5 514	−89.7	42.4	5 490	131	−99.6	−89.7
5^+	6 404	23.8	37.8	6 363	469	−85.6	23.6
$2^-(5)$	7 977	−90.7	39.7	7 941	136	−99.4	−90.7
6^+	8 014	29.4	36.8	7 964	497	−84.5	29.2
7^+	9 700	34.3	35.8	9 641	523	−83.4	34.0
$3^-(7)$	10 450	−91.7	37.2	10 401	140	−99.1	−91.7
8^+	11 452	38.6	34.8	11 383	548	−82.3	38.3
$4^-(9)$	12 932	−92.7	34.7	12 871	145	−98.8	−92.7
9^+	13 262	42.5	33.9	13 183	572	−81.2	42.3
10^+	15 123	46.4	33.0	15 035	595	−80.1	46.1
$5^-(11)$	15 422	−93.7	32.3	15 349	150	−98.6	−93.7
11^+	17 030	50.4	32.2	16 933	617	−78.9	50.1
$6^-(13)$	17 916	−94.7	30.1	17 831	154	−98.3	−94.6
12^+	18 978	55.0	31.3	18 871	639	−77.6	54.7

TABLE II. Vibronically averaged isotropic hfcc and the aa and bb–cc components of the anisotropic hf tensor in $K=1$ vibronic species of the $1\,^2\Pi_u$ electronic state of CH_2^+. Superscripts $+$ and $-$ in the first column denote the levels belonging predominantly to the $X\,^2A_1$ and $A\,^2B_1$ electronic states, respectively. For a key to the notation see Table I.

| | $^{12}CH_2^+$ | | | | $^{13}CH_2^+$ | | | | |
| | | H | | | | ^{13}C | | | H |
v_2 ($K=1$)	E (cm^{-1})	A_{iso} (MHz)	A_{aa} (MHz)	$A_{bb}-A_{cc}$ (MHz)	E (cm^{-1})	A_{iso} (MHz)	A_{aa} (MHz)	$A_{bb}-A_{cc}$ (MHz)	A_{iso} (MHz)
0^+	72	−0.557	42.7	33.3	71	348	−90.8	286	−0.555
1^+	993	−24.7	43.7	34.9	988	294	−93.2	294	−24.6
2^+	1 780	−23.2	43.1	35.0	1 770	303	−92.6	292	−23.4
3^+	2 849	−0.182	41.0	33.9	2 831	374	−89.5	283	−0.433
4^+	4 078	−27.7	41.3	34.3	4 055	310	−92.3	292	−25.7
$0^-(2)$	4 317	−46.2	42.0	34.8	4 296	247	−94.9	300	−48.4
5^+	5 642	18.7	38.4	33.4	5 606	448	−86.4	274	18.4
$1^-(4)$	6 702	−84.6	40.9	33.0	6 672	151	−98.9	313	−84.4
6^+	7 222	22.3	37.4	33.4	7 177	469	−85.6	272	21.9
7^+	8 840	26.3	36.4	33.4	8 786	494	−84.6	269	26.4
$2^-(6)$	9 208	−84.9	38.3	30.5	9 165	157	−98.5	313	−85.3
8^+	10 574	35.5	35.3	33.7	10 509	532	−82.9	265	35.2
$3^-(8)$	11 675	−90.0	35.9	27.9	11 620	150	−98.7	315	−89.9
9^+	12 360	39.0	34.3	33.7	12 286	555	−81.9	262	38.7
$4^-(10)$	14 119	−37.0	33.5	28.8	14 045	354	−90.2	289	−28.0
10^+	14 239	−11.5	33.4	30.5	14 163	378	−89.1	285	−20.6
11^+	16 071	47.0	32.6	33.9	15 979	602	−79.6	256	46.8
$5^-(12)$	16 665	−92.5	31.2	23.2	16 586	157	−98.2	315	−92.6
12^+	18 002	52.1	31.7	33.9	17 901	626	−78.3	252	51.7
$6^-(14)$	19 159	−94.1	29.0	21.0	19 060	160	−98.0	316	−94.0
13^+	19 971	56.9	30.9	33.8	19 860	647	−77.1	249	56.4

TABLE III. Computed vibronic mean values for the isotropic hfcc in $\Omega=1/2$ and $\Omega=3/2$ components of the $K=1$ levels in the $1\,^2\Pi$ electronic state of CH₂⁺. For a key to the notation see Tables I and II.

v_2 (K=1)	ΔS.O. (cm⁻¹)	¹²CH₂⁺ A_{iso}(H) (MHz)		¹³CH₂⁺ A_{iso}(¹³C) (MHz)	
		$\Omega=1/2$	$\Omega=3/2$	$\Omega=1/2$	$\Omega=3/2$
0⁺	3.2	−0.389	−0.731	349	348
1⁺	13.8	−24.2	−25.2	295	292
2⁺	13.6	−23.6	−22.7	302	304
3⁺	2.3	−0.467	0.091	373	375
4⁻	−10.7	−28.1	−27.1	308	312
0⁻(2)	9.7	−45.6	−46.9	249	245
5⁺	0.0	18.5	18.8	448	449
1⁻(4)	−2.7	−84.1	−85.1	152	149
6⁺	3.0	21.9	22.7	468	471
7⁺	−3.2	25.7	26.9	492	495
2⁻(6)	2.6	−84.3	−85.6	158	155
8⁺	0.0	35.3	35.6	532	533
3⁻(8)	−1.1	−89.8	−90.2	151	149
9⁺	1.3	38.8	39.2	554	555
4⁻(10)	−7.7	−36.2	−37.7	354	353
10⁺	7.7	−12.2	−10.7	378	379
11⁺	−1.0	46.8	47.2	601	602
5⁻(12)	0.7	−92.3	−92.7	158	157
12⁺	0.0	52.0	52.1	626	627
6⁻(14)	−0.5	−93.9	−94.2	160	160
13⁺	0.6	56.8	57.0	647	648

tensor on the bond angle is presented in Figs. 2–4. The molecule is assumed to lie in the yz plane, $x \equiv c$, $y \equiv a$, $z \equiv b$. As in the previous study on NH₂ we neglect the matrix element $A_{bc}(\epsilon B_1)$ which is nondiagonal with respect to the two electronic states in question for both the C and H atoms, as well as $A_{ac}(\epsilon A'')$ for the H atom which connects the states $^2A'$ and $^2A''$ correlating (in the lower C_s point group) to $^2A_1$ and $^2B_1$ of C_{2v}, respectively. The terms $A_{ac}(\epsilon A_2)$ and $A_{ab}(\epsilon B_2)$ for the carbon atom vanish by symmetry.

For the electronic isotropic hfcc both the results obtained with and without the B_K correction are shown in Fig. 2. The largest differences between the two sets of results are found for the carbon atom in the $A\,^2B_1$ electronic state (10–15 MHz, i.e., about 5%–10%), in all other cases the discrepancies do not exceed 4 MHz. As expected the B_K correction does not significantly affect the results for the components of the anisotropic hf tensor.

The treatment applied in the present study for calculation of the electronic hfcc's is of a very similar level of sophistication as that employed for the investigation of the ground state of the CH molecule.[8] Since in the latter case extensive experimental information on the hfcc's was available, it was possible to estimate the magnitude of the calculational errors. Assuming that they do not differ much for CH and CH₂⁺ we expect that the present results for the electronic isotropic hfcc are accurate to within 2%–3% at the linear nuclear arrangement and even more at the bent

TABLE IV. Vibronic mean values for the isotropic hfcc in the $K=0$ and $K=1$ levels of CHD⁺. For key to notation see also Tables I and II.

	$K=0$					$K=1$			
	¹²CHD⁺		¹³CHD⁺			¹²CHD⁺		¹³CHD⁺	
		H		¹³C			H		¹³C
v_2	E (cm⁻¹)	A_{iso} (MHz)	E (cm⁻¹)	A_{iso} (MHz)	v_2	E (cm⁻¹)	A_{iso} (MHz)	E (cm⁻¹)	A_{iso} (MHz)
0⁺	0	−0.958	0	346	0⁺	61	−0.214	61	348
1⁺	889	−7.17	882	339	1⁺	891	−21.0	886	302
2⁺	1 848	−2.50	1 833	360	2⁺	1 568	−28.6	1 559	286
0⁻(1)	2 855	−88.6	2 843	125	3⁺	2 430	−5.58	2 411	355
3⁺	2 928	5.61	2 904	391	4⁺	3 506	1.35	3 478	383
4⁻	4 121	13.1	4 088	421	0⁻(2)	3 903	−79.1	3 883	156
1⁻(3)	5 029	−89.5	5 002	130	5⁺	4 772	13.9	4 733	428
5⁺	5 406	19.5	5 363	449	6⁺	6 010	−31.8	5 968	318
6⁺	6 768	25.1	6 714	475	1⁻(4)	6 168	−34.7	6 127	279
2⁻(5)	7 207	−90.4	7 166	134	7⁺	7 479	26.2	7 420	483
7⁺	8 196	30.0	8 132	500	2⁻(6)	8 281	−88.1	8 233	145
3⁻(7)	9 391	−91.3	9 337	138	8⁺	8 943	30.5	8 873	505
8⁺	9 681	34.3	9 607	522	9⁺	10 403	−12.8	10 330	409
9⁺	11 217	38.1	11 133	545	3⁻(8)	10 521	−42.3	10 453	266
4⁻(9)	11 582	−92.1	11 513	142	10⁺	12 005	38.9	11 915	552
10⁺	12 798	41.7	12 704	566	4⁻(10)	12 674	−91.1	12 598	149
5⁻(11)	13 778	−93.0	13 696	147	11⁺	13 611	42.7	13 510	574
11⁺	14 421	45.1	14 315	587	5⁻(12)	14 868	−90.9	14 778	158
6⁻(13)	15 978	−93.9	15 882	151	12⁺	15 255	44.5	15 145	588
12⁺	16 079	48.6	15 964	607	13⁺	16 914	40.7	16 795	591
13⁺	17 771	52.3	17 645	626	6⁻(14)	17 086	−84.4	16 983	179
7⁻(15)	18 180	−94.8	18 072	155	14⁺	18 631	53.6	18 500	633
14⁺	19 493	56.5	19 357	646	7⁻(16)	19 281	−94.2	19 166	160

TABLE V. Vibronic mean values for the isotropic hfcc in the $K=0$ and $K=1$ levels of CD2+. For key to notation see also Tables I and II.

	$K=0$					$K=1$			
	¹²CD2+		¹³CD2+			¹²CD2+		¹³CD2+	
		D		¹³C			H		¹³C
v_2	E (cm⁻¹)	A_{iso} (MHz)	E (cm⁻¹)	A_{iso} (MHz)	v_2	E (cm⁻¹)	A_{iso} (MHz)	E (cm⁻¹)	A_{iso} (MHz)
0⁺	0	−0.155	0	345	0⁺	46	0.0194	46	348
1⁺	733	−1.37	726	332	1⁺	763	−2.43	757	314
2⁺	1 496	−1.06	1 481	344	2⁺	1 347	−5.02	1 336	274
3⁺	2 349	0.0519	2 323	371	3⁺	1 984	−2.13	1 964	328
0⁻(1)	2 617	−13.6	2 603	125	4⁺	2 825	0.0192	2 794	373
4⁺	3 294	1.16	3 257	399	0⁻(2)	3 478	−12.1	3 454	157
5⁺	4 316	2.14	4 268	424	5⁺	3 828	0.503	3 786	388
1⁻(3)	4 469	−13.7	4 437	128	6⁺	4 854	2.20	4 800	429
6⁺	5 403	2.99	5 343	448	1⁻(4)	5 372	−13.1	5 332	142
2⁻(5)	6 321	−13.8	6 273	132	7⁺	5 977	3.08	5 912	453
7⁺	6 544	3.74	6 472	470	8⁺	7 112	0.974	7 038	423
8⁺	7 733	4.40	7 650	492	2⁻(6)	7 258	−10.7	7 199	184
3⁻(7)	8 175	−13.9	8 110	136	9⁺	8 346	4.56	8 257	499
9⁺	8 964	5.00	8 869	512	3⁻(8)	9 092	−13.7	9 019	145
4⁻(9)	10 033	−14.0	9 952	139	10⁺	9 601	5.05	9 500	516
10⁺	10 233	5.53	10 126	531	11⁺	10 863	2.23	10 755	489
11⁺	11 536	6.03	11 418	550	4⁻(10)	10 976	−10.5	10 883	194
5⁻(11)	11 893	−14.2	11 796	143	12⁺	12 201	6.14	12 077	556
12⁺	12 870	6.49	12 740	568	5⁻(12)	12 820	−14.0	12 714	149
6⁻(13)	13 755	−14.3	13 643	146	13⁺	13 551	6.62	13 415	574
13⁺	14 232	6.93	14 090	585	6⁻(14)	14 679	−13.8	14 558	161
7⁻(15)	15 619	−14.4	15 491	150	14⁺	14 930	6.67	14 783	582
14⁺	15 619	7.38	15 466	603	15⁺	16 319	7.13	16 161	603
15⁺	17 030	7.85	16 865	619	7⁻(16)	16 553	−13.9	16 417	161
8⁻(17)	17 483	−14.5	17 340	153	16⁺	17 745	8.02	17 575	626
16⁺	18 462	8.36	18 286	636	8⁻(18)	18 413	−14.4	18 263	158
9⁻(19)	19 347	−14.6	19 190	157	17⁺	19 188	8.57	19 007	642
17⁺	19 914	8.94	19 727	652					

geometries. The errors of the anisotropic hfcc's should be even smaller.

Our results calculated at a bond angle of 140° and a C–H distance of 1.092 Å are in very good agreement with those of Knight *et al.*[11] obtained at a slightly different geometry ($\angle$HCH$=139.3°$, C–H$=1.087$ Å). We obtain for the isotropic hfcc values of 355 and 4.5 MHz (353 and 6 MHz without B_K correction) for ¹³C and H, respectively. The corresponding numbers of Knight *et al.* are 355.9 and 6.3 MHz. [Note that the angular dependence of the isotropic hfcc for the hydrogen atom in the $X\,^2A_1$ state is very strong, particularly in the bond angle region of 140° (Fig. 2). Our B_K value at the bond angle of 139.3° (for which the calculations in Ref. 8 were done) taken from the curve presented in Fig. 2 coincides almost exactly with that given by Knight *et al.*] Knight *et al.* also published the results of calculations for the *xx* and *zz* components of the anisotropic hf tensor: $A_{xx}(c)=-96.8$, $A_{zz}(c)=186.6$, $A_{xx}(H)=-39.5$, $A_{zz}(H)=-7.7$ MHz. For the carbon atom they are identical to our values (-97, 187 MHz), and for the hydrogen center the agreement is very reasonable (-38, -5 MHz).

The angular dependence of the electronic hfcc's in the 1 $^2\Pi_u$ state of CH2+ is similar to that found for the corresponding state of NH2³ (note that the ordering of the elec-

tronic states is reversed, the $^2A_1$ being the ground state in CH2+). So, for example, the isotropic hfcc in the $^2A_1$ state for both C and H centers increase strongly upon bending reflecting an increase in σ character of the singly occupied $3a_1$ orbital. The small absolute value for the isotropic hfcc of the hydrogen atom at the equilibrium geometry of the $X\,^2A_1$ state is a consequence of the interplay between the direct contribution from the $3a_1$ orbital (positive sign) and negative correlation contributions arising from the spin polarization of the doubly occupied shell by the unpaired electron. Similar effects were found in the NH2 molecule.³ The components of the anisotropic hf tensor for the carbon atom, particularly those corresponding to the $^2B_1$ state, show weak dependence on the bond angle. Differences in behavior of the electronic hfcc's in CH2+ and NH2 are caused by different electronic configurations of the corresponding states of CH2+ and NH2, the latter possessing in addition a doubly occupied b_1 orbital in the $^2A_1$ electronic state and $(3a_1)^2$ in the $^2B_1$ state.

The results of calculations of the vibronic mean values for the experimentally accessible components of the hf tensor in the $K=0$ and $K=1$ levels of the 1 $^2\Pi_u$ electronic state of various isotopomers of CH2 in the energy range up to 20 000 cm⁻¹ are presented in Tables I–V. Vibrational averaging is performed only over the bending vibrations
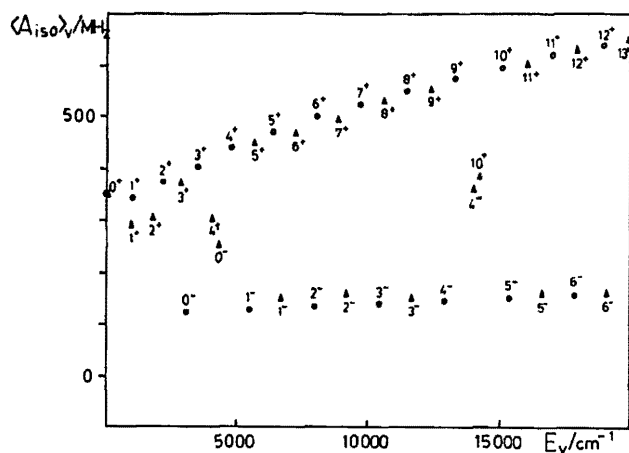
FIG. 5. Computed vibronic mean values for the isotropic hfcc of the carbon atom in the $1\,^2\Pi_u$ electronic state of CH_2^+. Circles denote $K=0$ vibronic levels belonging to the $X\,^2A_1$ state (O) and $A\,^2B_1$ electronic state (●). Triangles correspond to the $K=1$ vibronic levels; Δ: levels belonging predominantly to the $X\,^2A_1$ electronic state, $\blacktriangle$: levels of the $A\,^2B_1$ state. v_2^{bent} quantum numbers are given. The superscripts + and − denote the $X\,^2A_1$ and $A\,^2B_1$ electronic states, respectively.

because it has been found that the correction due to averaging over the zeroth vibrational state in the stretching modes is insignificant in the present case. All numbers are given with three significant digits (in spite of the fact that the estimated absolute calculation error is of the order of magnitude of 1 MHz) to enable comparison of the results for various isotopomers. We give only the results which are needed for the discussion of various effects to follow; the complete tables can be obtained upon request. The variation of the vibronic isotopic hfcc's for ^{13}C in $^{13}CH_2$ and H in $^{12}CH_2$ with the bending quantum number is graphically presented in Figs. 5 and 6.

As stated in the introductory part of this study and as discussed in detail in Ref. 4 the most important cause for
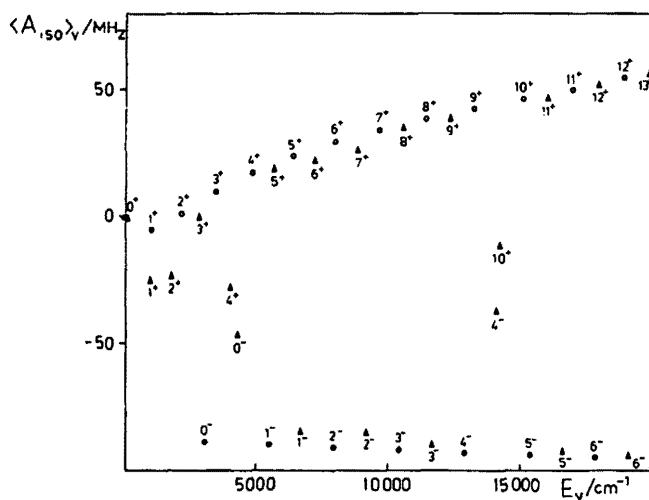

FIG. 6. Vibronic mean values for the isotropic hfcc of the hydrogen atom in the $1\,^2\Pi_u$ electronic state of CH_2^+. For a key to the notation see Fig. 5.

discrepancy between the theoretically obtained values for the vibronic hfcc's and their experimentally derived counterparts seems to be the inaccuracy in calculation of the energetic position of the vibronic levels, particularly of those which are strongly coupled with each other. In the case of NH_2 (Ref. 4) it was possible to study this effect quantitatively because accurate potential surfaces derived by fitting of experimental data were available.[35] This analysis showed that, in spite of the fact that the differences between the positions of the corresponding vibronic levels obtained, employing two sets of potentials (ab initio and experimentally derived) in the energy range between 0 and 20 000 cm⁻¹ amounted to roughly 1000 cm⁻¹, the discrepancies between the values of the vibronic hfcc's were generally smaller than 3% for $K=0$ levels which are vibronically uncoupled.[5] The situation is quite different for the $K\neq0$ levels. In the vicinity of the barrier to linearity and particularly where the above mentioned near degeneracies occur they are strongly shared between both the $^2B_1$ and $^2A_1$ potential surfaces and the differences in the positions of the vibronic levels significantly affect the agreement between the corresponding calculated hfcc's. This should be kept in mind when considering the results given in Tables I-V of the present study. However, because of the substantially lower barrier to linearity in the ground electronic state of CH_2^+ (compared to NH_2) the critical region around the barrier is described much better (the error by calculation of the vibronic level position is estimated to be of the order of a few ten wave numbers[26]) and we expect that our results also for $K=1$ levels are quite reliable there. This does not hold for the nearly degenerate levels lying in the high energy region (for example $v_2=10^+$ and $v_2=4$, see Table II and Figs. 5 and 6) where much larger errors in the calculated vibronic energies and consequently much poorer description of the vibronic mixing is expected. Larger relative errors in the vibronic isotropic hfcc for the $^2A_1$ electronic state are possible in the low energy region for the hydrogen atom due to the small absolute value of the electronic hfcc (becoming zero at a bond angle of roughly 140°, Fig. 2).

In Table III are presented the results of calculations of the isotropic hfcc's for $\Omega=1/2$ and $\Omega=3/2$ components of the $K=1$ levels in CH_2^+. The absolute differences between the corresponding pairs of numbers are not large (smaller than 3 MHz), but significant relative differences occur for the hydrogen atom in low lying vibronic levels due to the above-mentioned behavior of the electronic hfcc function.

We do not feel it necessary to discuss in more detail the results presented in Tables I-V and Figs. 5 and 6. Let us only stress that the calculated ratio of the vibronic hfcc for the deuterium and hydrogen atoms in $^{12}CD_2^+$ and $^{12}CH_2^+$ in the lowest $K=0$ level (Tables I and V) is 0.256, i.e., it differs significantly from the ratio of the respective g_N values (0.1535), representing a nice example for the effect of a low barrier to linearity for the $^2A_1$ state connected with the strong geometry dependence of the electronic hfcc on the vibronically averaged values of the hfcc. This trend is even more pronounced in the lowest $K=1$ levels (com-

puted ratio $CD_2^+/CH_2^+ = -0.035$) due to the additional effect of the Renner–Teller coupling.

V. CONCLUSION

In this study we present the results of pure *ab initio* calculations of the vibronically averaged hfcc's in various isotopomers of CH_2^+. In spite of some inherent difficulties, particularly the description of the phenomena in the regions of strong vibronic coupling, we feel that our predictions will be of use for future experimental investigations of the spectra of this radical.

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[1] M. Perić, B. Engels, and S. D. Peyerimhoff, J. Mol. Spectrosc. **150**, 56 (1991).

[2] M. Perić, B. Engels, and S. D. Peyerimhoff, J. Mol. Spectrosc. **150**, 70 (1991).

[3] B. Engels, M. Perić, W. Reuter, S. D. Peyerimhoff, and F. Grein, J. Chem. Phys. **96**, 4526 (1992).

[4] M. Perić and B. Engels, J. Chem. Phys. (in press).

[5] R. Renner, Z. Phys. **92**, 172 (1934).

[6] T. Sears, Comput. Phys. Reports **2**, 1 (1984).

[7] B. Engels, Chem. Phys. Lett. **179**, 398 (1991).

[8] B. Engels (submitted for publication).

[9] D. Feller and E. R. Davidson, Theor. Chim. Acta **68**, 57 (1985).

[10] Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. **2**, 751 (1968).

[11] L. B. Knight, Jr., M. Winiski, P. Miller, C. A. Arrington, and D. Feller, J. Chem. Phys. **91**, 4468 (1989).

[12] M. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, J. Mol. Spectrosc. **153**, 738 (1992).

[13] W. A. Lathan, K. J. Hahre, and J. A. Pople, J. Am. Chem. Soc. **93**, 808 (1971).

[14] S. Sakai, S. Kato, K. Morokuma, and I. Kusonoki, Chem. Phys. **75**, 5398 (1981).

[15] R. Bartholomae, D. Martin, and B. T. Sutcliffe, J. Mol. Spectrosc. **87**, 367 (1981).

[16] R. Jaquet and V. Staemmler, Chem. Phys. **68**, 479 (1982).

[17] S. Carter and N. C. Handy, J. Mol. Spectrosc. **95**, 9 (1982).

[18] J. Tennyson and B. T. Sutcliffe, J. Mol. Spectrosc. **101**, 71 (1983).

[19] S. Carter, N. C. Handy, and B. T. Sutcliffe, Mol. Phys. **49**, 745 (1983).

[20] S. Carter and N. C. Handy, Mol. Phys. **52**, 1367 (1984).

[21] D. J. De Frees and A. D. McLean, J. Chem. Phys. **82**, 333 (1985).

[22] B. T. Sutcliffe and J. Tennyson, Mol. Phys. **58**, 1053 (1986).

[23] B. T. Sutcliffe and J. Tennyson, J. Chem. Soc. Faraday Trans. 2, **83**, 1663 (1987).

[24] S. G. Walters, F. Penotti, J. Geratt, and M. Raimondi, Mol. Phys. **61**, 1341 (1987).

[25] J. S. Lee and D. Secrest, J. Phys. Chem. **92**, 1821 (1988).

[26] W. Reuter and S. D. Peyerimhoff, Chem. Phys. **160**, 11 (1992).

[27] F. B. van Duijnefeld, Technical Report RJ 945, IBM Research Laboratory, San Jose.

[28] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).

[29] I. Carmichael, J. Chem. Phys. **91**, 1072 (1989).

[30] (a) R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974); *ibid.* **39**, 217 (1974); (b) R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. **35**, 771 (1978); (c) R. J. Buenker and R. A. Phillips, J. Mol. Struct. **123**, 291 (1985).

[31] J. T. Hougen, P. R. Bunker, and J. W. C. Johns, J. Mol. Spectrosc. **34**, 136 (1972).

[32] P. R. Bunker and B. Landsberg, J. Mol. Spectrosc. **67**, 374 (1977).

[33] M. Perić, S. D. Peyerimhoff, and R. J. Buenker, Int. Rev. Phys. Chem. **4**, 85 (1985).

[34] Ch. Jungen and A. J. Merer, Mol. Phys. **40**, 1 (1980).

[35] Ch. Jungen, K.-E. J. Hallin, and A. J. Merer, Mol. Phys. **40**, 25 (1980).