Centrifugal Distortion Analysis of the Microwave and Millimeter Wave Spectra of Deuterated Ketenes[1,2]

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Measurements of R and Q branch a-type pure rotational transitions in the frequency range from 8 GHz to 220 GHz are reported for ketene-d_1 and ketene-d_2. The microwave and millimeter wave transitions were analysed in terms of Watson's reduced Hamiltonian, including the sextic terms H_{KJ} and H_{JK}. The values of the inertial defect and the τ defect obtained from the centrifugal distortion analysis are in accord with the planar model for the ketene molecule.

I. Introduction

The importance of ketene for synthetic work, coupled with the fact that it has a relatively simple and symmetric molecular structure, initiated spectroscopic investigations comparatively early. It was the subject of some of the earliest microwave studies [1–3].

The analysis of the infrared vibrational spectra [4] and the microwave studies of pure rotational transitions [1–3, 5] have given us information about the molecular geometry and confirmed the C_{2v} symmetry. Thus, relatively dependable rotational constants have been obtained for the H_2, HD and D_2 substituted species [1–4]. It has also been concluded on the basis of the vibrational and rotational spectra that the ketene molecule is planar. This conclusion came mostly from the symmetry properties of rotational and rotational-vibrational transitions. There has been only one paper, by Johns, Stone and Winnewisser [6], in which an inertial defect value for H_2 ketene could be derived from the combined analysis of infrared and microwave data.

In the present paper we attempt to fill some gaps in the knowledge about the deuterium substituted species. We have measured sufficient millimeter wave transitions to perform the centrifugal distortion analysis for both ketene-d_1 and ketene-d_2. These analyses have yielded, in addition to refined rotational constants, the quartic and sextic centrifugal distortion constants, values of the inertial defect and the τ defect. Comparison of these inertial defect values with values calculated from a normal coordinate analysis supports strongly the planar model for the ketene molecular structure.

The frequency predictions of pure rotational transitions together with their calculated standard deviations provide a basis for a possible search for interstellar deuterated ketene molecules.

II. Experimental Procedures

Both deuterated ketenes were prepared using a modified Hurd-lamp [7] by pyrolysing hexadeuteroacetone and partially deuterated acetone. In the process of producing ketene-d_1, following the method reported by Moore and Pimentel [4], both normal ketene and ketene-d_2 are also synthetized. We have not attempted to separate these species since in the vibrational ground state studies their presence has caused no problems. The pyrolysis of acetone gives a number of by-products apart from methane, principally CO_2 and ethylene. These molecules are, however, nonpolar and therefore their presence in the sample does not lead to disturbing lines in the rotational spectrum of the ketenes. However, in order to avoid pressure broadening of the ketene absorption lines a distillation procedure was applied to remove all of the heavy methane and CO_2, and most of the heavy ethylene.

The measurements of centimeter wave lines between 8 and 18 GHz, and between 24 and 36 GHz were carried out using a Hewlet-Packard 8460A Molecular Rotational Resonance spectrometer. A Stark modulation of frequency 33.33 kHz and a two meter X-band Stark cell were employed.

The millimeter wave range rotational transitions were measured by means of a spectrometer having

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a 2.5 meter free space absorption cell. The sources of radiation were different OKI klystrons in the frequency range 28 – 45 GHz. By means of harmonic multiplication the whole range between 50 and 250 GHz could be covered. In order to increase the precision of the measurements and the detectability of weak lines data acquisition utilizing a PDP-8/I computer was applied, as described by Winnewisser [8]. This system provides an enhanced signal-to-noise ratio by means of signal averaging and smoothing. Frequency determination is performed by the computer using a line-center calculation program [9]. The accuracy of these measurements is believed to be better than ± 20 kHz for the stronger lines.

Sample pressure in the room temperature cell was in the range $10 - 50 \cdot 10^{-3}$ Torr.

III. General Features of the Pure Rotational Spectra

The microwave and millimeter wave rotational spectra of the deuterated ketene molecules show the structure expected for *a*-type transitions of slightly asymmetric prolate top molecules. Although deuteration introduces more asymmetry than is the case for normal ketene, the asymmetry parameters do not change significantly. The value of $\varkappa$ is -0.99722, -0.99489 and -0.99144 for ketene-h_2, ketene-d_1 and ketene-d_2 respectively.

The appearance of the pure rotational spectra is governed by the small asymmetry and the sizeable centrifugal distortion effects. The intensities basically follow a prolate symmetric top intensity distribution, which is further regulated by nuclear spin statistics. For ketene-d_2 the statistical weight of the anti-symmetric levels is half that of the symmetric levels, so that transitions originating from levels of even K_a have half the weight of those originating from odd K_a levels.

Figure 1 compares the K_a pattern obtained for the three isotopically substituted ketenes for the transition $J = 9 \leftarrow 8$ (the data for ketene-h_2 were taken from the work of Johns, Stone and Winnewisser [6]). Deviations from the rigid-rotor pattern are

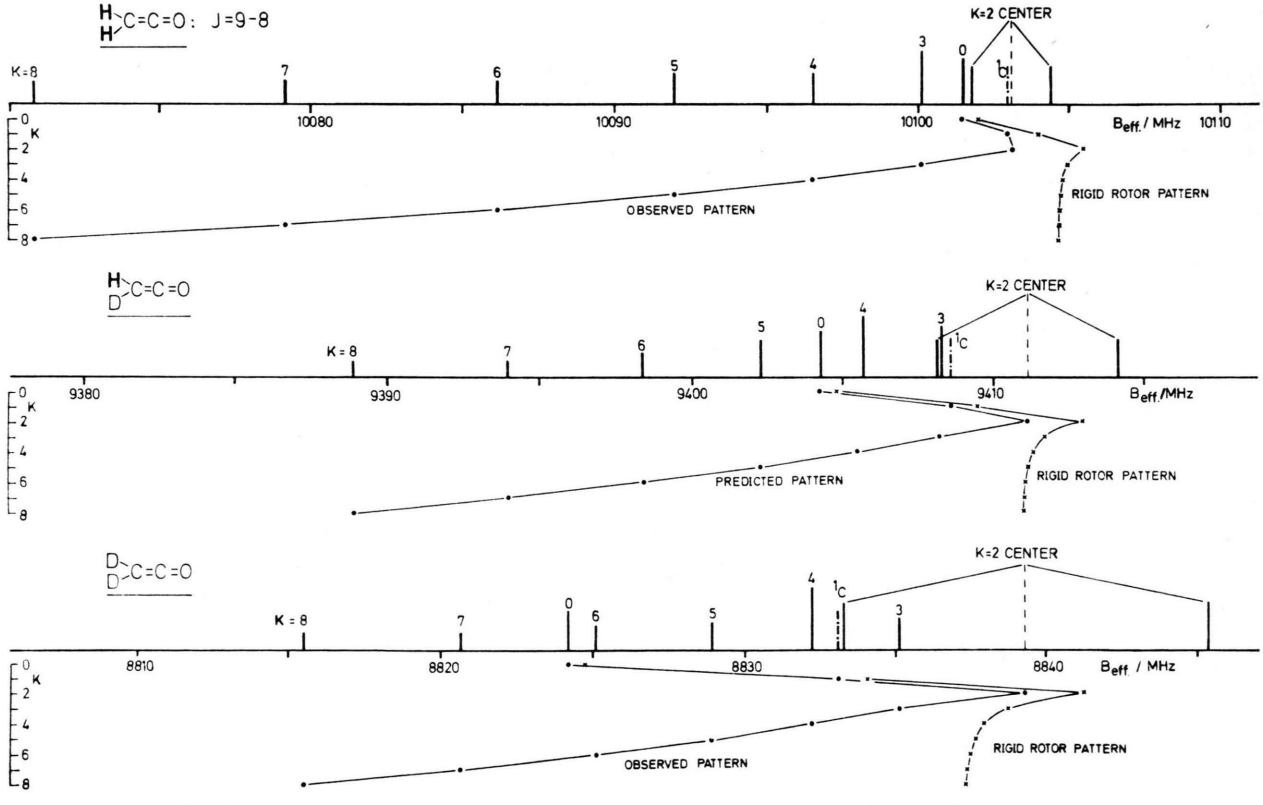

Fig. 1. The K_a patterns of typical *a*-type ^qRbranch pure rotational transitions for the ketene species.

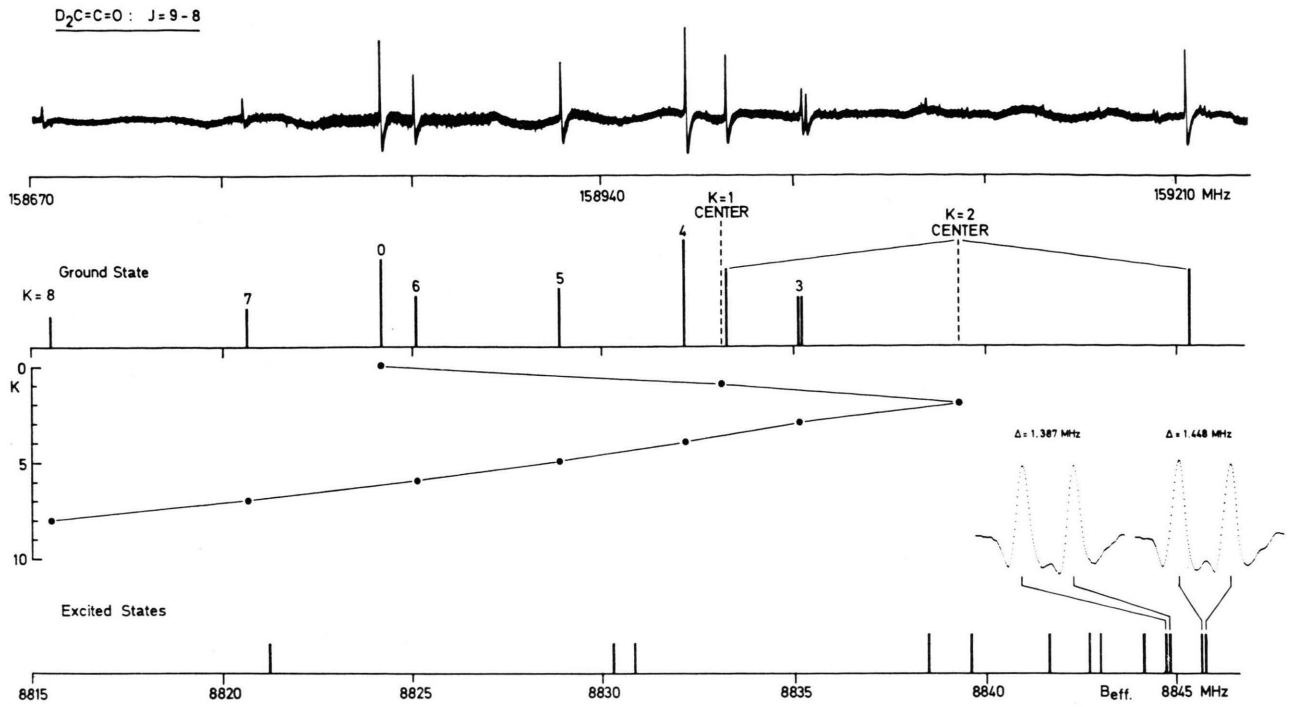

Fig. 2. Ground-state and excited state *a*-type ^{9}R branch rotational transitions of CD_2CO. Both upper scale, giving the frequency of ground state lines, and lower scale giving $B'_{\mathrm{eff}}=v/(2J+2)$ for excited state lines refer to the observed spectrum at the top of the Figure.

indicated. Thus it is seen that band heads are formed by the slight asymmetry, enhanced further by the centrifugal distortion effects. This enhancement is the smallest for ketene-d_2 since it is the heaviest and least symmetric of the three species. The regularity of the K_a pattern proved to be a great help in the spectral assignments.

On-line signal averaging and smoothing made it possible to observe weak vibrational satellites belonging to the three lowest frequency vibrational states. Figure 2 depicts a typical R-branch transition and indicates a few lines originating from excited vibrational states. It was possible to observe the very small $K_a=3$ asymmetry doubling in the ground vibrational state and also in the excited vibrational states. The inserts of Fig. 2 show a magnified view of these doublets as they actually appear on the screen of the oscilloscope. The analysis of these excited states will be published separately.

IV. Assignment of Rotational Transitions

The approximate assignment of the rotational spectra presented no difficulties since rigid rotor predictions were available [1, 2, 5, 10]. The number of a-type R branch transitions was 87, while there were 18 a-type Q branch transitions measured for ketene-d_2. For ketene-d_1 49 R branch transitions and 12 Q branch transitions have been measured and used in the least-squares calculations.

Approximate centrifugal distortion parameters were at our disposal as preliminary results of recent normal-coordinate calculations [11]. These we used in a simplified centrifugal distortion program utilizing Polo's expansion formulas [12], written for the PDP-8/I computer.

Further refinement was done through a bootstrap procedure using an asymmetric rotor fitting program described by Johns and Olson [13]. The bootstrap method consisted in the first stage of fitting the observed lines to quartic distortion constants only. Later it was found necessary to include two higher-order, sextic distortion constants, H_{JK} and H_{KJ}, to remove most of the residual errors. A discussion of the trends in the residual errors is given in Section VI.

V. Treatment of Centrifugal Distortion Effects

The centrifugal distortion analysis of the rotational spectra has been performed using Watson's reduced Hamiltonian operator formalism in the I^r-axis representation, constraining R_6 to zero. The form of the operator below indicates that, of the sextic distortion coefficients, only H_{KJ} and H_{JK} have been determined in our calculations [for the complete form, see Eq. (37) in Ref. [14]]:

$$H_{\mathrm{red}} = [1/2(\tilde{B}+\tilde{C})J^2 + \{\tilde{A} - 1/2(\tilde{B}+\tilde{C})\}J_a^2 - \Delta_J (J^2)^2 - \Delta_{JK} J^2 J_a^2 - \Delta_K J_a^4 + H_{JK}(J^2)^2 J_a^2 + H_{KJ} J^2 J_a^4]$$
$$+ [(J_b^2 - J_c^2)\{1/4(\tilde{B}-\tilde{C}) - \delta_J J^2 - \delta_K J_a^2\} + \{1/4(\tilde{B}-\tilde{C}) - \delta_J J^2 - \delta_K J_a^2\}(J_b^2 - J_c^2)]$$

where J, J_a, J_b and J_c are the operators for the total angular momentum and its components, and the square brackets indicate that the first group of operators is diagonal in K, while those in the second bracket are off-diagonal in K by two units. The form of the second bracket also indicates that J_a^2 does not commute with $(J_b^2 - J_c^2)$. The reduced rotational constants are given in Tables I and II for the two deuterated species of ketene.

Table I. Spectroscopic constants of CD_2CO for Watson's reduced Hamiltonian in the I^r axis representation [a].

$\tilde{A}$	141503.7	(3.4)	MHz
$\tilde{B}$	9121.2370	(37)	MHz
$\tilde{C}$	8552.2946	(37)	MHz
Δ_J	2.7085	(30)	kHz
Δ_{JK}	0.321389	(38)	MHz
Δ_K	4.3228	(fixed)	MHz
δ_J	0.21972	(50)	kHz
δ_K	0.2030	(19)	MHz
H_{JK}	2.97	(15)	Hz
H_{KJ}	−0.14188	(49)	kHz
$\tilde{\Delta} = \tilde{I}_c - \tilde{I}_a - \tilde{I}_b$	0.114457	(83)	amu·Å² [b]

$\tilde{\varkappa} = -0.991441$

[a] The standard deviation of the fit is 19.7 kHz. Numbers in parentheses are standard errors.

[b] The value of the conversion constant; const $= I_b$(amu·Å²) · B(MHz) used in this work is 505379; as calculated from the latest values of $h = 6.626176(36) \cdot 10^{-27}$ erg·sec and the Avogadro constant: $6.022045(31) \cdot 10^{23}$ mol^{-1} (Ref. [24]).

Since the difference $(A - \Delta_K)$ can be determined from a-type rotational transitions alone, but the two constants A and Δ_K separately cannot, we have applied the following procedure. The value of Δ_K was first fixed at an estimate provided by normal-coordinate analysis utilizing the normal frequencies of all three isotopically substituted ketene species, their available centrifugal distortion constants and some a-type Coriolis zeta coefficients. The transitions were then fitted to the given Hamiltonian and a first approximation was obtained for the quartic

Table II. Spectroscopic constants of CHDCO for Watson's reduced Hamiltonian in the I^r axis representation [a].

$\tilde{A}$	194352.2	(22.9)	MHz
$\tilde{B}$	9647.543	(15)	MHz
$\tilde{C}$	9174.166	(15)	MHz
Δ_J	3.1637	(67)	kHz
Δ_{JK}	0.326970	(77)	MHz
Δ_K	13.6709	(fixed)	MHz
δ_J	0.22525	(92)	kHz
δ_K	0.2392	(74)	MHz
H_{JK}	2.79	(40)	Hz
H_{KJ}	−0.2779	(14)	kHz
$\tilde{\Delta} = \tilde{I}_c - \tilde{I}_a - \tilde{I}_b$	0.10264	(30)	amu·Å² [b]

$\tilde{\varkappa} = -0.994889$

[a] The standard deviation of the fit is 23 kHz. Numbers in parentheses are standard errors.

[b] see footnote to Table I.

distortion constants. On the basis of these improved centrifugal distortion data another normal-coordinate analysis was made yielding now a modified Δ_K-value. In the end two of the sextic distortion coefficients were also used in the refinement calculations. A comparison of our final, converged set of distortion constants to the normal-coordinate results is given in Tables III and IV.

In this way we have obtained better determined values for the A rotational constant and for the

Table III. Comparison of least-squares values of quartic distortion coefficients of CD_2CO to the results of normal-coordinate calculations [a].

	L. S.		N.C.	
Δ_J	2.7085	(30)	2.652	kHz
Δ_{JK}	0.321389	(38)	0.33218	MHz
Δ_K	4.3228	(fixed)	4.6103	MHz
δ_J	0.21972	(50)	0.2194	kHz
δ_K	0.2030	(19)	0.202	MHz

[a] Although here the comparison is made between two sets corresponding to different values of Δ_K, the differences of N. C. calcd. values corresponding to slightly different Δ_K are within the standard errors for the L. S. values.

Table IV. Comparison of least-squares values of quartic distortion coefficients of CHDCO to the results of normal-coordinate calculations [a].

	L. S.	N. C.	
Δ_J	3.1637 (67)	3.160	kHz
Δ_{JK}	0.326970 (77)	0.33138	MHz
Δ_K	13.6709 (fixed)	14.4657	MHz
δ_J	0.22525 (92)	0.2283	kHz
δ_K	0.2392 (74)	0.238	MHz

[a] See footnote as for Table III.

Table V. Watsons's determinable spectroscopic constants for CD_2CO [MHz], $\tau_2^* = \tau_2/(\mathfrak{A}+\mathfrak{B}+\mathfrak{C})$.

		Norm. Coord. calc. values (Ref. 11)
$\mathfrak{A}$	141503.7 (3.4)	
$\mathfrak{B}$	9121.1574 (37)	
$\mathfrak{C}$	8553.0279 (37)	
τ'_{aaaa}	−18.58759 (16)	−19.78069
τ'_{bbbb}	−0.012592 (16)	−0.012365
τ'_{cccc}	−0.0090762 (79)	−0.008854
τ_1	−1.31806 (19)	
τ_2^*	−0.0793027 (77)	
$\Delta\tau$	−0.000114 (25)	

inertia defect than would have been possible from just the *a*-type rotational transitions. A better method for solving this problem would, of course, be a simultaneous fit to some perpendicular ro-vibrational infrared transitions together with the *a*-type rotational transitions. No higher-resolution ro-vibrational data is, however, available to date on the deuterated ketene species.

Table VI. Watson's determinable spectroscopic constants for CHDCO [MHz], $\tau_2^* = \tau_2/(\mathfrak{A}+\mathfrak{B}+\mathfrak{C})$.

		Norm. Coord. calc. values (Ref. 11)
$\mathfrak{A}$	194352.2 (22.9)	
$\mathfrak{B}$	9647.398 (15)	
$\mathfrak{C}$	9174.978 (15)	
τ'_{aaaa}	−56.00414 (34)	−59.20114
τ'_{bbbb}	−0.014457 (34)	−0.014464
τ'_{cccc}	−0.010853 (19)	−0.010811
τ_1	−1.34585 (39)	
τ_2^*	−0.068273 (31)	
$\Delta\tau$	−0.000040 (63) [undefined!]	

VI. Discussion

a) Discussion of the Results of Centrifugal Distortion Analysis

It is possible to transform the spectroscopic constants obtained as Watson's determinable combinations of the Kivelson-Wilson quartic coefficients to calculate the so-called derived spectroscopic constants: A, B, C, τ'_{aabb}, $\hbar^4\tau_{abab}$, τ'_{bbcc} and τ'_{ccaa} [14]. This transformation involves the use of planarity conditions, rigorously valid only for equilibrium values of the quartic distortion coefficients. These planarity conditions were originally given by Dowling [15], and by Oka and Morino [16, 17]. We shall use these and similar planarity constraints following Kirchhoff [18] and Cook et al. [19, 20] to provide several alternative sets of derived parameters. The following treatment is outlined in a paper by Yamada and Winnewisser [21] and the present results are contained in Tables VII and VIII. The equations following

Table VII. Spectroscopic constants derived from determinable parameters via different planarity conditions for CD_2CO [a].

Version	1	2	3	4	5	Norm. Coord. calc. (Ref. 11)	
A	141503.7 (3.4)	141503.7 (3.4)	141503.7 (3.4)	141503.7 (3.4)	141503.7 (3.4)		MHz
B	9121.1855 (37)	9121.1855 (38)	9121.2045 (37)	9121.1855 (37)	9121.1951 (37)		MHz
C	8552.3460 (37)	8552.3473 (38)	8552.3270 (37)	8552.3459 (37)	8552.3364 (37)		MHz
I_A	3.571489 (85)	3.571489 (85)	3.571489 (85)	3.571489 (85)	3.571489 (85)		amu·Å²
I_B	55.407162 (25)	55.407162 (26)	55.407046 (24)	55.407161 (25)	55.407103 (25)		amu·Å²
I_C	59.092441 (25)	59.092432 (26)	59.092572 (24)	59.092441 (25)	59.092507 (25)		amu·Å²
Δ	0.113790 (38)	0.113781 (37)	0.114036 (82)	0.113790 (38)	0.113915 (60)		amu·Å²
τ'_{aabb}	−1.36380 (78)	−1.36128 (34)	−1.4017 (75)	−1.36396 (81)	−1.3831 (43)		MHz
τ'_{bbcc}	−0.010556 (11)	−0.010556 (11)	−0.010556 (11)	−0.010394 (17)	−0.0104760 (26)	−0.010317	MHz
τ'_{ccaa}	0.05630 (61)	0.05630 (60)	0.0942 (73)	0.05630 (60)	0.0755 (40)	0.0649	MHz
$\hbar^4\tau_{aabb}$	0.14125 (69)	0.14125 (68)	0.14125 (68)	0.14125 (69)	0.1631 (45)	0.1572	MHz
$\hbar^4\tau_{abab}$	−0.75253 (73)	−0.75127 (51)	−0.7715 (41)	−0.75261 (75)	−0.7731 (44)	−0.7861	MHz
$R_6 \times 10^6$	−8.69	−8.69	−8.69	−13.8	−11.2		MHz
$S_{111} \times 10^8$	6.12	6.12	6.12	9.7	7.9		

[a] see footnote to Table I.

Table VIII. Spectroscopic constants derived from determinable parameters via different planarity conditions for CHDCO [a].

Version	1	2	3	4	5	Norm. Coord. calc. (Ref. 11)	
A	194352.2 (22.9)	194352.2 (22.9)	194352.2 (22.9)	194352.2 (22.9)	194352.2 (22.9)		MHz
B	9647.476 (14)	9647.476 (15)	9647.490 (15)	9647.476 (15)	9647.483 (15)		MHz
C	9174.233 (14)	9174.234 (15)	9174.219 (15)	9174.233 (15)	9174.226 (15)		MHz
I_A	2.60033 (31)	2.60033 (31)	2.60033 (31)	2.60033 (31)	2.60033 (31)		amu·Å²
I_B	52.384582 (88)	52.384582 (91)	52.384504 (85)	52.384582 (88)	52.384542 (86)		amu·Å²
I_C	55.086785 (88)	55.086780 (91)	55.086871 (85)	55.086785 (88)	55.086829 (86)		amu·Å²
Δ	0.10188 (14)	0.10187 (14)	0.10204 (30)	0.10188 (14)	0.10196 (22)		amu·Å²
τ'_{aabb}	−1.4895 (24)	−1.48800 (96)	−1.518 (30)	−1.4896 (24)	−1.504 (16)		MHz
τ'_{bbcc}	−0.012384 (26)	−0.012384 (26)	−0.012384 (26)	−0.012310 (44)	−0.0123477 (80)	−0.012350	MHz
τ'_{ccaa}	0.1560 (20)	0.1560 (20)	0.185 (29)	0.1560 (20)	0.171 (16)	0.1711	MHz
$\hbar^4\tau_{aabb}$	0.3105 (22)	0.3105 (22)	0.3105 (22)	0.3105 (22)	0.327 (18)	0.3372	MHz
$\hbar^4\tau_{abab}$	−0.9000 (23)	−0.8992 (16)	−0.914 (16)	−0.9000 (23)	−0.915 (17)	−0.9297	MHz
$R_6 \times 10^6$	−8.47	−8.47	−8.47	−10.8	−9.6		MHz
$S_{111} \times 10^8$	7.18	7.18	7.18	9.1	8.1		

[a] see footnote to Table I.

from the planarity conditions are summarized here for the different versions 1 through 5 (see also Yamada and Winnewisser [21]).

Version 1

These planarity equations are obtainable from those of Dowling [15] and have the following form:

$$\hbar^4\tau_{aabb} = 1/2\left[-\frac{B^2}{A^2}\tau'_{aaaa} - \frac{A^2}{B^2}\tau'_{bbbb} + \frac{A^2B^2}{C^4}\tau'_{cccc}\right],$$

$$\tau'_{bbcc} = 1/2\left[-\frac{B^2C^2}{A^4}\tau'_{aaaa} + \frac{C^2}{B^2}\tau'_{bbbb} + \frac{B^2}{C^2}\tau'_{cccc}\right],$$

$$\tau'_{aacc} = 1/2\left[+\frac{C^2}{A^2}\tau'_{aaaa} - \frac{A^2C^2}{B^4}\tau'_{bbbb} + \frac{A^2}{C^2}\tau'_{cccc}\right].$$

In terms of these quantities the rest of the derived constants are calculated from:

$$\hbar^4\tau_{abab} = [\tau_1 - (\hbar^4\tau_{aabb} + \tau'_{bbcc} + \tau'_{aacc})]/2,$$

$$\tau'_{aabb} = \hbar^4(\tau_{aabb} + 2\tau_{abab}),$$

and the τ defect, as derived from Eq. (67) in Watson's paper [14] is:

$$\Delta\tau = \tau'_{cccc} - (\tau_2 - C\tau_1)/(A+B).$$

The τ defect is a rather sensitive function of τ_2. τ_1 and τ_2 were calculated according to

$$\tau_1 = \tau'_{aabb} + \tau'_{bbcc} + \tau'_{aacc}$$

and

$$\tau_2 = -2(2A - B - C)\Delta_J + 4(B-C)(\delta_J + \delta_K) - 2(B+C)(\Delta_{JK} + 3\Delta_J),$$

which is identical to the equation for τ_2 in Cook, De Lucia and Helminger [22] (see Table VI there).

Version 2

The quantities $\hbar^4\tau_{aabb}$, τ'_{bbcc} and τ'_{aacc} are as in Version 1, but:

$$\hbar^4\tau_{abab} = \{\tau_2 - (A\tau'_{bbcc} + B\tau'_{aacc} + C\hbar^4\tau_{aabb})\}/2C.$$

Version 3

The quantities $\hbar^4\tau_{aabb}$, τ'_{bbcc} and $\hbar^4\tau_{abab}$ are as in Version 1 and 2, while τ'_{aacc} is given by

$$\tau'_{aacc} = \{\tau'_{cccc} - \Delta\tau - \tau'_{bbcc}(A-C)/(A+B)\}\frac{A+B}{B-C}.$$

Version 4

The quantities $\hbar^4\tau_{aabb}$ and τ'_{ccaa} and $\hbar^4\tau_{abab}$ are as in Version 1, but:

$$\tau'_{bbcc} = \left\{\tau'_{cccc} - \Delta\tau - \tau'_{aacc}\left(\frac{B-C}{A+B}\right)\right\}\frac{A+B}{A-C}.$$

Version 5

Here $\hbar^4\tau_{abab}$ is calculated as in Version 1, while the rest of the quartic constants are obtained from:

$$\hbar^4\tau_{aabb} = \left[-(\tau_1 - \tau_2/C)/C - \frac{A-C}{B^2}\tau'_{bbbb} - \frac{B-C}{A^2}\tau'_{aaaa}\right]\Big/ \left(\frac{A-C}{A^2} + \frac{B-C}{B^2}\right),$$

$$\tau'_{bbcc} = C^2\left\{\frac{\hbar^4\tau_{aabb}}{A^2} + \frac{\tau'_{bbbb}}{B^2}\right\},$$

$$\tau'_{aacc} = C^2\left\{\frac{\tau'_{aaaa}}{A^2} + \frac{\hbar^4\tau_{aabb}}{B^2}\right\}.$$

TABLE IX. OBSERVED AND CALCULATED FREQUENCIES OF DOCCO IN MHZ

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
** A TYPE R BRANCH **							
1(0, 1) -	0(0, 0)	17673.5720(1.0)	17673.5208(0.0009)	0.0512	0.590	0.000	
2(0, 2) -	1(0, 1)	35345.1620(1.0)	35345.1569(0.0017)	0.0051	1.769	0.590	
2(1, 1) -	1(1, 0)	35913.8190(1.0)	35913.8139(0.0017)	0.0051	6.222	5.024	
2(1, 2) -	1(1, 1)	34777.5710(1.0)	34777.5673(0.0017)	0.0037	6.165	5.005	
3(0, 3) -	2(0, 2)	53013.0360(1.0)	53013.0237(0.0025)	0.0123	3.537	1.769	
3(1, 2) -	2(1, 1)	53869.4140(1.0)	53869.4158(0.0024)	-0.0018	8.019	5.222	
3(1, 3) -	2(1, 2)	52165.3500(1.0)	52165.0758(0.0024)	-0.0258	7.905	6.165	Ref. 25
3(2, 1) -	2(2, 0)	53019.8460(1.0)	53019.8556(0.0021)	-0.0096	21.236	19.467	
3(2, 2) -	2(2, 1)	53012.5830(1.0)	53012.5768(0.0021)	0.0062	21.235	19.467	
4(0, 4) -	3(0, 3)	70675.2453(1.0)	70675.2374(0.0031)	0.0079	5.894	3.537	
4(1, 3) -	3(1, 2)	71823.4592(1.0)	71823.4464(0.0030)	0.0128	10.415	8.019	
4(1, 4) -	3(1, 3)	69551.0648(1.0)	69551.0593(0.0030)	0.0055	10.225	7.905	
4(2, 2) -	3(2, 1)	70699.9342(1.0)	70699.9458(0.0026)	-0.0116	23.594	21.236	
4(2, 3) -	3(2, 2)	70681.7524(1.0)	70681.7499(0.0026)	0.0025	23.593	21.235	
4(3, 1) -	3(3, 0)		70673.8281(0.0025)		45.709	43.352	
4(3, 2) -	3(3, 1)	70673.8173(1.0)	70673.8063(0.0025)	0.0110	45.709	43.352	
5(0, 5) -	4(0, 4)	88329.9366(1.0)	88329.9161(0.0036)	0.0205	8.841	5.894	
5(1, 4) -	4(1, 3)	89775.3875(1.0)	89775.3737(0.0034)	0.0138	13.409	10.415	
5(1, 5) -	4(1, 4)	86935.2158(1.0)	86935.0178(0.0034)	-0.0020	13.125	10.225	
5(2, 3) -	4(2, 2)	88385.8603(1.0)	88385.8660(0.0030)	-0.0057	26.542	23.594	
5(2, 4) -	4(2, 3)	88349.4655(1.0)	88349.4781(0.0030)	-0.0126	26.540	23.593	
5(3, 2) -	4(3, 1)	88343.5072(0.0)	88343.5751(0.0028)	-0.0679	48.656	45.709	
5(3, 3) -	4(3, 2)	88343.5072(1.0)	88343.4990(0.0028)	0.0082	48.656	45.709	
5(4, 1) -	4(4, 0)	88318.4834(1.0)	88318.4963(0.0036)	-0.0129	79.606	76.660	
5(4, 2) -	4(4, 1)		88318.4963(0.0036)		79.606	76.660	
6(0, 6) -	5(0, 5)	105975.1769(1.0)	105975.1824(0.0039)	-0.0055	12.376	8.841	
6(1, 5) -	5(1, 4)	107724.6618(1.0)	107724.6581(0.0036)	0.0037	17.003	13.409	
6(1, 6) -	5(1, 5)	104316.4567(1.0)	104316.4587(0.0036)	-0.0020	16.605	13.125	
6(2, 4) -	5(2, 3)	106079.3735(1.0)	106079.0674(0.0032)	0.0061	30.081	26.542	
6(2, 5) -	5(2, 4)	106015.4106(1.0)	106015.4001(0.0032)	0.0105	30.076	26.540	
6(3, 3) -	5(3, 2)	106014.1123(0.0)	105014.2020(0.0030)	-0.0897	52.192	48.656	
6(3, 4) -	5(3, 3)	106014.1123(0.0)	106013.9991(0.0030)	0.1132	52.192	48.656	
6(4, 2) -	5(4, 1)		105982.8855(0.0038)		83.141	79.606	
6(4, 3) -	5(4, 2)	105982.8734(1.0)	105982.8854(0.0038)	-0.0120	83.141	79.606	
6(5, 1) -	5(5, 0)	105945.7836(1.0)	105945.7938(0.0054)	-0.0102	122.911	119.377	
6(5, 2) -	5(5, 1)		105945.7938(0.0054)		122.911	119.377	
7(0, 7) -	6(0, 6)	123609.1589(1.0)	123609.1674(0.0043)	-0.0085	16.499	12.376	
7(1, 6) -	6(1, 5)	125670.7664(1.0)	125670.7513(0.0037)	0.0151	21.195	17.003	
7(1, 7) -	6(1, 6)	121694.9049(1.0)	121694.8983(0.0037)	0.0066	20.664	16.605	
7(2, 5) -	6(2, 4)	123781.0053(1.0)	123780.9924(0.0033)	0.0134	34.210	30.081	
7(2, 6) -	6(2, 5)	123679.1583(1.0)	123679.1549(0.0034)	0.0031	34.202	30.076	
7(3, 4) -	6(3, 3)	123685.6782(0.0)	123685.9050(0.0030)	-0.2268	56.318	52.192	
7(3, 5) -	6(3, 4)	123685.4397(1.0)	123685.4485(0.0030)	-0.0088	56.318	52.192	
7(4, 3) -	6(4, 2)		123647.6513(0.0040)		87.265	83.141	
7(4, 4) -	6(4, 3)	123647.6443(1.0)	123647.6505(0.0040)	-0.0062	87.265	83.141	
7(5, 2) -	6(5, 1)		123603.6938(0.0055)		127.034	122.911	
7(5, 3) -	6(5, 2)	123603.7011(1.0)	123603.6938(0.0055)	0.0073	127.034	122.911	
7(6, 1) -	6(6, 0)		123551.3572(0.0072)		175.608	171.487	
7(6, 2) -	6(6, 1)		123551.3572(0.0072)		175.608	171.487	
8(0, 8) -	7(0, 7)	141230.0299(1.0)	141230.0165(0.0049)	0.0133	21.210	16.499	
8(1, 7) -	7(1, 6)	143613.1993(1.0)	143613.0936(0.0037)	0.0062	25.985	21.195	
8(1, 8) -	7(1, 7)	139069.9503(1.0)	139069.8639(0.0037)	-0.0136	25.303	20.664	
8(2, 6) -	7(2, 5)	141493..6211(1.0)	141493.0695(0.0034)	-0.0074	38.929	34.210	
8(2, 7) -	7(2, 6)	141340.3872(1.0)	141340.3816(0.0035)	0.0056	38.917	34.202	
8(3, 5) -	7(3, 4)	141358.8762(1.0)	141358.8909(0.0029)	-0.0147	61.033	56.318	
8(3, 6) -	7(3, 5)	141357.9575(1.0)	141357.9779(0.0030)	-0.0204	61.033	56.318	
8(4, 4) -	7(4, 3)	141312.8373(1.0)	141312.8563(0.0039)	-0.0190	91.979	87.265	
8(4, 5) -	7(4, 4)	141312.8373(1.0)	141312.8544(0.0039)	-0.0171	91.979	87.265	
8(5, 3) -	7(5, 2)	141261.7115(1.0)	141261.7173(0.0053)	-0.0058	131.746	127.034	
8(5, 4) -	7(5, 3)		141261.7173(0.0053)		131.746	127.034	
8(6, 2) -	7(6, 1)	141201.4496(1.0)	141201.4396(0.0066)	0.0100	180.318	175.608	
8(6, 3) -	7(6, 2)		141201.4396(0.0066)		180.318	175.608	
8(7, 1) -	7(7, 0)	141130.8054(0.0)	141130.7062(0.0086)	0.0992	237.677	232.970	
8(7, 2) -	7(7, 1)		141130.7062(0.0086)		237.677	232.970	
9(0, 9) -	8(0, 8)	158835.9907(1.0)	158835.9975(0.0050)	-0.0069	26.508	21.210	
9(1, 8) -	8(1, 7)	161551.1103(1.0)	161551.1128(0.0038)	-0.0028	31.374	25.985	
9(1, 9) -	8(1, 8)	156440.8934(1.0)	156440.8949(0.0039)	-0.0015	30.521	25.303	
9(2, 7) -	8(2, 6)	159216.7170(1.0)	159216.7041(0.0038)	0.0129	44.240	38.929	
9(2, 8) -	8(2, 7)	158998.7141(1.0)	158998.7194(0.0039)	-0.0053	44.220	38.917	
9(3, 6) -	8(3, 5)	159033.3625(1.0)	159033.3795(0.0029)	-0.0170	66.338	61.033	
9(3, 7) -	8(3, 6)	159031.7017(1.0)	159031.7059(0.0030)	-0.0042	66.338	61.033	
9(4, 5) -	8(4, 4)	158978.5485(1.0)	158978.5638(0.0039)	-0.0153	97.282	91.979	
9(4, 6) -	8(4, 5)		158978.5591(0.0039)		97.282	91.979	
9(5, 4) -	8(5, 3)	158919.8775(1.0)	158919.8819(0.0052)	-0.0044	137.047	131.746	
9(5, 5) -	8(5, 4)		158919.8819(0.0052)		137.047	131.746	
9(6, 3) -	8(6, 2)	158851.5039(1.0)	158851.4774(0.0059)	0.0265	185.617	180.318	
9(6, 4) -	8(6, 3)		158851.4774(0.0059)		185.617	180.318	
9(7, 2) -	8(7, 1)	158771.5993(1.0)	158771.5625(0.0071)	0.0373	242.973	237.677	
9(7, 3) -	8(7, 2)		158771.5625(0.0071)		242.973	237.677	
9(8, 1) -	8(8, 0)	158679.1422(1.0)	158679.1711(0.0128)	-0.0289	309.093	303.800	
9(8, 2) -	8(8, 1)		158679.1711(0.0128)		309.093	303.800	
10(0,10) -	9(0, 9)	176425.0058(1.0)	176425.0114(0.0079)	-0.0056	32.393	26.508	
10(1, 9) -	9(1, 8)	179484.2395(1.0)	179484.2218(0.0043)	0.0177	37.361	31.374	
10(1,10) -	9(1, 9)		173807.5450(0.0048)		36.319	30.521	
10(2, 8) -	9(2, 7)	176953.7673(1.0)	176953.2589(0.0047)	-0.0011	50.143	44.240	
10(2, 9) -	9(2, 8)	176653.8225(1.0)	176653.8078(0.0049)	0.0147	50.113	44.220	
10(3, 7) -	9(3, 6)	176709.5925(1.0)	176709.6057(0.0033)	-0.0132	72.233	66.338	
10(3, 8) -	9(3, 7)	176706.7263(1.0)	176706.7369(0.0034)	-0.0109	72.232	66.338	
10(4, 6) -	9(4, 5)	176644.8133(1.0)	176644.8371(0.0042)	-0.0241	103.174	97.282	
10(4, 7) -	9(4, 6)		176644.8269(0.0042)		103.174	97.282	
10(5, 5) -	9(5, 4)	176578.2082(1.0)	176578.2053(0.0054)	0.0029	142.937	137.047	
10(5, 6) -	9(5, 5)		176578.2053(0.0054)		142.937	137.047	
10(6, 4) -	9(6, 3)	176501.5027(1.0)	176501.4650(0.0059)	0.0377	191.504	185.617	
10(6, 5) -	9(6, 4)		176501.4650(0.0059)		191.504	185.617	
10(7, 3) -	9(7, 2)	176412.2952(1.0)	175412.2489(0.0065)	0.0463	248.858	242.973	
10(7, 4) -	9(7, 3)		176412.2489(0.0065)		248.858	242.973	
10(8, 2) -	9(8, 1)	176309.3006(1.0)	176309.3342(0.0126)	-0.0336	314.974	309.093	
10(8, 3) -	9(8, 2)		176309.3342(0.0126)		314.974	309.093	

TABLE IX. OBSERVED AND CALCULATED FREQUENCIES OF DDCCO IN MHZ (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
10(9, 1) -	9(9, 0)		176191.8533(0.0267)		389.827	383.950	
10(9, 2) -	9(9, 1)		176191.8533(0.0267)		389.827	383.950	
11(0,11) -	10(0,10)		193995.6049(0.0107)		38.864	32.393	
11(1,10) -	10(1, 9)		197411.8163(0.0057)		43.946	37.361	
11(1,11) -	10(1,10)		191169.3838(0.0065)		42.696	36.319	
11(2, 9) -	10(2, 8)		194704.0896(0.0064)		56.637	50.143	
11(2,10) -	10(2, 9)		194305.2865(0.0065)		56.594	50.113	
11(3, 8) -	10(3, 7)		194387.8205(0.0044)		78.717	72.233	
11(3, 9) -	10(3, 8)		194383.1595(0.0045)		78.716	72.232	
11(4, 7) -	10(4, 6)		194311.7393(0.0051)		109.656	103.174	
11(4, 8) -	10(4, 7)		194311.7196(0.0051)		109.656	103.174	
11(5, 6) -	10(5, 5)		194236.7151(0.0067)		149.416	142.937	
11(5, 7) -	10(5, 6)		194236.7050(0.0067)		149.416	142.937	
11(6, 5) -	10(6, 4)		194151.3968(0.0078)		197.981	191.504	
11(6, 6) -	10(6, 5)		194151.3968(0.0078)		197.981	191.504	
11(7, 4) -	10(7, 3)		194052.7461(0.0094)		255.331	248.858	
11(7, 5) -	10(7, 4)		194052.7461(0.0094)		255.331	248.858	
11(8, 3) -	10(8, 2)		193939.2269(0.0157)		321.443	314.974	
11(8, 4) -	10(8, 3)		193939.2269(0.0157)		321.443	314.974	
11(9, 2) -	10(9, 1)		193809.8010(0.0306)		396.292	389.827	
11(9, 3) -	10(9, 2)		193809.8013(0.0306)		396.292	389.827	
11(10, 1) -	10(10, 0)		193663.5902(0.0555)		479.847	473.387	
11(10, 2) -	10(10, 1)		193663.5902(0.0555)		479.847	473.387	
12(0,12) -	11(0,11)	211545.9918(1.0)	211545.9875(0.0144)	0.0043	45.920	38.864	
12(1,11) -	11(1,10)	215333.2782(1.0)	215333.2758(0.0079)	0.0024	51.128	43.946	
12(1,12) -	11(1,11)		208525.9981(0.0092)		49.651	42.696	
12(2,10) -	11(2, 9)	212470.4473(1.0)	212470.4293(0.0088)	0.0180	63.725	56.637	
12(2,11) -	11(2,10)	211952.9336(1.0)	211952.7961(0.0089)	0.0375	63.664	56.594	
12(3, 9) -	11(3, 8)	212068.2765(1.0)	212058.2943(0.0053)	-0.0175	85.791	78.717	
12(3,10) -	11(3, 9)	212061.3403(1.0)	212061.0451(0.0064)	-0.0048	85.790	78.716	
12(4, 8) -	11(4, 7)	211979.2867(1.0)	211979.3363(0.0070)	-0.0499	116.727	109.656	
12(4, 9) -	11(4, 8)		211979.2984(0.0070)		116.726	109.656	
12(5, 7) -	11(5, 6)	211895.4079(1.0)	211895.3988(0.0093)	0.0091	156.484	149.416	
12(5, 8) -	11(5, 7)		211895.3987(0.0093)		156.484	149.416	
12(6, 6) -	11(6, 5)	211801.7917(0.3)	211801.2671(0.0119)	0.5246	205.046	197.981	
12(6, 7) -	11(6, 6)		211801.2671(0.0119)		205.046	197.981	
12(7, 5) -	11(7, 4)	211693.0363(1.0)	211693.0354(0.0155)	0.0009	262.392	255.331	
12(7, 6) -	11(7, 5)		211693.0354(0.0155)		262.392	255.331	
12(8, 4) -	11(8, 3)	211568.7432(0.3)	211568.8221(0.0230)	-0.0789	328.500	321.443	
12(8, 5) -	11(8, 4)		211568.8221(0.0230)		328.500	321.443	
12(9, 3) -	11(9, 2)		211427.3951(0.0384)		403.344	395.292	
12(9, 4) -	11(9, 3)		211427.3951(0.0384)		403.344	396.292	
12(10, 2) -	11(10, 1)		211267.7445(0.0647)		486.894	479.847	
12(10, 3) -	11(10, 2)		211267.7445(0.0647)		486.894	479.847	
12(11, 1) -	11(11, 0)		211088.9218(0.1044)		579.117	572.076	
12(11, 2) -	11(11, 1)		211088.9218(0.1044)		579.117	572.076	
** A TYPE Q BRANCH **							
1(1, 0) -	1(1, 1)		568.1286(0.0003)		5.024	5.005	
2(1, 1) -	2(1, 2)		1704.3752(0.0008)		6.222	6.165	
3(1, 2) -	3(1, 3)	3408.7500(1.0)	3408.7151(0.0015)	0.0349	8.019	7.935	Ref. 26
4(1, 3) -	4(1, 4)	5681.1200(1.0)	5681.1022(0.0025)	0.0178	10.415	10.225	Ref. 26
5(1, 4) -	5(1, 5)	8521.4700(1.0)	8521.4581(0.0035)	0.0119	13.409	13.125	
6(1, 5) -	6(1, 6)	11929.6730(1.0)	11929.6575(0.0046)	0.0154	17.003	16.605	
7(1, 6) -	7(1, 7)	15905.5460(1.0)	15905.5105(0.0056)	0.0355	21.195	20.664	
8(1, 7) -	8(1, 8)	20448.7100(1.0)	20448.7402(0.0068)	-0.0302	25.985	25.303	Ref. 3
9(1, 8) -	9(1, 9)	25558.9300(1.0)	25558.9582(0.0080)	-0.0282	31.374	30.521	Ref. 3
10(1, 9) -	10(1,10)	31235.6033(1.0)	31235.6350(0.0097)	-0.0320	37.361	36.319	
11(1,10) -	11(1,11)	37478.0970(1.0)	37478.0681(0.0123)	0.0289	43.946	42.696	
12(1,11) -	12(1,12)		44285.3458(0.0163)		51.128	49.651	
13(1,12) -	13(1,13)		51656.3080(0.0221)		58.909	57.185	
14(1,13) -	14(1,14)		59589.5036(0.0303)		67.286	65.299	
15(1,14) -	15(1,15)		68083.1445(0.0412)		76.261	73.990	
16(1,15) -	16(1,16)		77135.0569(0.0552)		85.832	83.260	
10(2, 8) -	10(2, 9)		899.3207(0.0017)		50.143	50.113	
11(2, 9) -	11(2,10)		1298.1239(0.0023)		56.637	56.594	
12(2,10) -	12(2,11)		1815.7570(0.0030)		63.725	63.664	
13(2,11) -	13(2,12)		2473.2484(0.0038)		71.405	71.323	
14(2,12) -	14(2,13)		3293.0612(0.0046)		79.679	79.569	
15(2,13) -	15(2,14)		4298.9645(0.0055)		88.548	88.404	
16(2,14) -	16(2,15)		5515.8782(0.0064)		98.011	97.828	
17(2,15) -	17(2,16)		6969.6899(0.0072)		108.071	107.838	
18(2,16) -	18(2,17)	8687.0555(1.0)	8687.0463(0.0079)	0.0092	118.727	118.437	
19(2,17) -	19(2,18)	10695.1293(1.0)	10695.1181(0.0084)	0.0109	129.979	129.623	
20(2,18) -	20(2,19)	13021.3590(1.0)	13021.3430(0.0087)	0.0160	141.830	141.396	
21(2,19) -	21(2,20)	15693.1720(1.0)	15693.1503(0.0087)	0.0217	154.279	153.756	
22(2,20) -	22(2,21)	18737.6200(1.0)	18737.6742(0.0085)	-0.0542	167.327	166.792	Ref. 3
23(2,21) -	23(2,22)	22181.3600(0.0)	22181.4618(0.0085)	-0.1018	180.975	180.235	Ref. 3
24(2,22) -	24(2,23)	26050.1700(1.0)	26050.1854(0.0084)	-0.0154	195.224	194.355	Ref. 3
25(2,23) -	25(2,24)	30368.3850(1.0)	30368.3659(0.0105)	0.0191	210.073	209.060	
26(2,24) -	26(2,25)	35159.1210(1.0)	35159.1182(0.0153)	0.0028	225.523	224.350	

TABLE X. OBSERVED AND CALCULATED FREQUENCIES OF HDCO IN MHZ

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
** A TYPE R BRANCH **							
1(0, 1) -	0(0, 0)	18821.6900(1.0)	18821.6965(0.0116)	-0.0065	0.628	0.000	Ref. 3
2(0, 2) -	1(0, 1)	37642.4107(1.0)	37642.4154(0.0030)	-0.0054	1.883	0.628	Ref. 27
2(1, 1) -	1(1, 0)	38114.4007(1.0)	38114.4221(0.0029)	-0.0221	8.076	6.804	Ref. 27
2(1, 2) -	1(1, 1)	37169.7500(0.0)	37169.5942(0.0029)	0.1558	8.028	6.788	Ref. 27
3(0, 3) -	2(0, 2)		56461.1791(0.0043)		3.767	1.883	
3(1, 2) -	2(1, 1)		57170.8725(0.0041)		9.983	8.076	
3(1, 3) -	2(1, 2)		55753.6588(0.0041)		9.888	8.028	
3(2, 1) -	2(2, 0)		56460.5195(0.0036)		28.435	26.552	
3(2, 2) -	2(2, 1)		56456.9130(0.0036)		28.435	26.552	
4(0, 4) -	3(0, 3)	75277.0089(1.0)	75277.0105(0.0052)	-0.0016	6.278	3.767	
4(1, 3) -	3(1, 2)	76226.3983(1.0)	76226.4086(0.0049)	-0.0103	12.525	9.983	
4(1, 4) -	3(1, 3)	74336.8458(1.0)	74336.8458(0.0050)	0.0054	12.368	9.888	
4(2, 2) -	3(2, 1)	75283.8424(1.0)	75283.8676(0.0044)	-0.0252	30.946	28.435	
4(2, 3) -	3(2, 2)	75274.8425(1.0)	75274.8514(0.0044)	-0.0089	30.946	28.435	
4(3, 1) -	3(3, 0)		75264.0966(0.0044)		61.760	59.250	
4(3, 2) -	3(3, 1)	75264.0773(1.0)	75264.0902(0.0044)	-0.0129	61.760	59.250	
5(0, 5) -	4(0, 4)	94088.9362(1.0)	94088.9325(0.0059)	0.0035	9.416	6.278	
5(1, 4) -	4(1, 3)	95280.7366(1.0)	95280.7233(0.0055)	0.0133	15.703	12.525	
5(1, 5) -	4(1, 4)	92918.8712(1.0)	92918.8654(0.0055)	0.0058	15.467	12.368	
5(2, 3) -	4(2, 2)	94109.9186(1.0)	94109.9360(0.0048)	-0.0174	34.086	30.946	
5(2, 4) -	4(2, 3)	94091.9961(1.0)	94091.9048(0.0048)	-0.0087	34.084	30.946	
5(3, 2) -	4(3, 1)	94080.4121(1.0)	94080.4373(0.0048)	-0.0252	64.898	61.760	
5(3, 3) -	4(3, 2)	94080.4121(1.0)	94080.4149(0.0048)	-0.0028	64.898	61.760	
5(4, 1) -	4(4, 0)	94055.8946(1.0)	94055.9010(0.0067)	-0.0064	107.999	104.862	
5(4, 2) -	4(4, 1)		94055.9010(0.0067)		107.999	104.862	
6(0, 6) -	5(0, 5)	112895.9813(1.0)	112895.9697(0.0065)	0.0116	13.182	9.416	
6(1, 5) -	5(1, 4)	114333.5180(1.0)	114333.5074(0.0056)	0.0106	19.517	15.703	
6(1, 6) -	5(1, 5)	111499.4474(1.0)	111499.4296(0.0057)	0.0178	19.186	15.467	
6(2, 4) -	5(2, 3)	112939.4183(1.0)	112939.4035(0.0051)	0.0147	37.853	34.086	
6(2, 5) -	5(2, 4)	112907.8453(1.0)	112907.8520(0.0051)	-0.0062	37.851	34.084	
6(3, 3) -	5(3, 2)	112896.9943(1.0)	112896.9943(0.0050)	-0.0312	68.664	64.898	
6(3, 4) -	5(3, 3)	112896.9637(1.0)	112896.9351(0.0050)	0.0286	68.664	64.898	
6(4, 2) -	5(4, 1)		112866.9585(0.0070)		111.764	107.999	
6(4, 3) -	5(4, 2)	112866.9313(1.0)	112866.9585(0.0070)	-0.0267	111.764	107.999	
6(5, 1) -	5(5, 0)	112829.5553(1.0)	112829.5302(0.0099)	0.0250	167.112	163.348	
6(5, 2) -	5(5, 1)		112829.5302(0.0099)		167.112	163.348	
7(0, 7) -	6(0, 6)		131697.1477(0.0074)		17.575	13.182	
7(1, 6) -	6(1, 5)		133384.4489(0.0056)		23.966	19.517	
7(1, 7) -	6(1, 6)		130078.2536(0.0056)		23.525	19.186	
7(2, 5) -	6(2, 4)		131772.9474(0.0054)		42.248	37.853	
7(2, 6) -	6(2, 5)		131722.4719(0.0055)		42.244	37.851	
7(3, 4) -	6(3, 3)		131713.8185(0.0049)		73.058	68.664	
7(3, 5) -	6(3, 4)		131713.6840(0.0049)		73.058	68.664	
7(4, 3) -	6(4, 2)		131677.9491(0.0070)		116.156	111.764	
7(4, 4) -	6(4, 3)		131677.9490(0.0070)		116.156	111.764	
7(5, 2) -	6(5, 1)		131633.9473(0.0095)		171.503	167.112	
7(5, 3) -	6(5, 2)		131633.9473(0.0095)		171.503	167.112	
7(6, 1) -	6(6, 0)		131580.2192(0.0128)		239.048	234.659	
7(6, 2) -	6(6, 1)		131580.2192(0.0128)		239.048	234.659	
8(0, 8) -	7(0, 7)	150491.4939(1.0)	150491.4954(0.0094)	-0.0016	22.595	17.575	
8(1, 7) -	7(1, 6)	152433.2392(1.0)	152433.2328(0.0060)	0.0064	29.051	23.966	
8(1, 8) -	7(1, 7)	148655.0827(1.0)	148655.0554(0.0059)	0.0273	28.484	23.525	
8(2, 6) -	7(2, 5)	150611.2471(1.0)	150611.2415(0.0063)	0.0055	47.272	42.248	
8(2, 7) -	7(2, 6)	150535.5629(1.0)	150535.5434(0.0064)	0.0195	47.266	42.244	
8(3, 5) -	7(3, 4)	150530.8213(0.0)	150530.9606(0.0050)	-0.1388	78.070	73.058	
8(3, 6) -	7(3, 5)	150530.8213(0.0)	150530.6915(0.0050)	0.1303	78.079	73.058	
8(4, 4) -	7(4, 3)	150488.8599(1.0)	150488.8616(0.0070)	-0.0017	121.176	116.156	
8(4, 5) -	7(4, 4)		150488.8613(0.0070)		121.176	116.156	
8(5, 3) -	7(5, 2)	150438.1526(1.0)	150438.1316(0.0088)	0.0210	176.521	171.503	
8(5, 4) -	7(5, 3)		150438.1316(0.0088)		176.521	171.503	
8(6, 2) -	7(6, 1)	150376.5193(1.0)	150376.5036(0.0104)	0.0157	244.064	239.048	
8(6, 3) -	7(6, 2)		150376.5036(0.0104)		244.064	239.048	
8(7, 1) -	7(7, 0)	150302.8722(1.0)	150302.8877(0.0185)	-0.0155	323.746	318.733	
8(7, 2) -	7(7, 1)		150302.8877(0.0185)		323.746	318.733	
9(0, 9) -	8(0, 8)		169278.0457(0.0129)		28.241	22.595	
9(1, 8) -	8(1, 7)		171479.5404(0.0075)		34.771	29.051	
9(1, 9) -	8(1, 8)		167229.5571(0.0075)		34.062	28.484	
9(2, 7) -	8(2, 6)		169454.9558(0.0085)		52.925	47.272	
9(2, 8) -	8(2, 7)		169346.8455(0.0086)		52.915	47.266	
9(3, 6) -	8(3, 5)		169348.4771(0.0059)		83.728	78.079	
9(3, 7) -	8(3, 6)		169347.9840(0.0060)		83.728	78.079	
9(4, 5) -	8(4, 4)		169299.6848(0.0077)		126.823	121.176	
9(4, 6) -	8(4, 5)		169299.6840(0.0077)		126.823	121.176	
9(5, 4) -	8(5, 3)		169242.0496(0.0092)		182.166	176.521	
9(5, 4) -	8(5, 3)		169242.0495(0.0092)		182.166	176.521	
9(6, 3) -	8(6, 2)		169172.4320(0.0090)		249.707	244.064	
9(6, 4) -	8(6, 3)		169172.4320(0.0090)		249.707	244.064	
9(7, 2) -	8(7, 1)		169089.4545(0.0158)		329.386	323.746	
9(7, 3) -	8(7, 2)		169089.4545(0.0158)		329.386	323.746	
9(8, 1) -	8(8, 0)		168992.0573(0.0393)		421.132	415.495	
9(8, 2) -	8(8, 1)		168992.0573(0.0393)		421.132	415.495	
10(0,10) -	9(0, 9)	188055.8119(1.0)	188055.8381(0.0181)	-0.0262	34.514	28.241	
10(1, 9) -	9(1, 8)		190523.0489(0.0106)		41.126	34.771	
10(1,10) -	9(1, 9)	185801.4949(1.0)	185801.4850(0.0109)	0.0099	40.260	34.062	
10(2, 8) -	9(2, 7)	188304.7756(1.0)	188304.7540(0.0121)	0.0216	59.206	52.925	
10(2, 9) -	9(2, 8)	188156.1741(1.0)	188156.1575(0.0123)	0.0166	59.191	52.915	
10(3, 7) -	9(3, 6)	188166.4063(1.0)	188166.4286(0.0083)	-0.0223	90.004	83.728	
10(3, 8) -	9(3, 7)	188165.5416(1.0)	188165.5833(0.0084)	-0.0417	90.004	83.728	
10(4, 6) -	9(4, 5)	188110.3759(1.0)	188110.4075(0.0100)	-0.0316	133.098	126.823	
10(4, 7) -	9(4, 6)		188110.4057(0.0100)		133.098	126.823	
10(5, 5) -	9(5, 4)	188045.6949(1.0)	188045.6680(0.0123)	0.0269	188.439	182.166	
10(5, 6) -	9(5, 5)		188045.6680(0.0123)		188.439	182.166	
10(6, 4) -	9(6, 3)	187967.9770(1.0)	187967.9598(0.0131)	0.0172	255.977	249.707	
10(6, 5) -	9(6, 4)		187967.9598(0.0131)		255.977	249.707	
10(7, 3) -	9(7, 2)	187875.5539(1.0)	187875.5645(0.0190)	-0.0107	335.653	329.386	
10(7, 4) -	9(7, 3)		187875.5645(0.0190)		335.653	329.386	
10(8, 2) -	9(8, 1)	187766.7849(0.0)	187767.2304(0.0423)	-0.4456	427.395	421.132	
10(8, 3) -	9(8, 2)		187767.2304(0.0423)		427.395	421.132	

TABLE X. OBSERVED AND CALCULATED FREQUENCIES OF HDCCO IN MHZ (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
10(9, 1) -	9(9, 0)		187641.7826(0.0967)		531.121	524.862	
10(9, 2) -	9(9, 1)		187641.7826(0.0967)		531.121	524.862	
** A TYPE Q BRANCH **							
1(1, 0) -	1(1, 1)		472.4193(0.0004)		6.804	6.788	
2(1, 1) -	2(1, 2)		1417.2472(0.0012)		8.076	8.028	
3(1, 2) -	3(1, 3)		2834.4608(0.0024)		9.983	9.888	
4(1, 3) -	4(1, 4)		4724.0236(0.0037)		12.525	12.368	
5(1, 4) -	5(1, 5)		7085.8816(0.0052)		15.703	15.467	
6(1, 5) -	6(1, 6)	9919.9850(1.0)	9919.9594(0.0067)	0.0256	19.517	19.186	
7(1, 6) -	7(1, 7)	13226.2053(1.0)	13226.1547(0.0082)	0.0503	23.966	23.525	
8(1, 7) -	8(1, 8)	17004.3653(1.0)	17004.3320(0.0099)	0.0330	29.051	28.484	}
9(1, 8) -	9(1, 9)	21254.3100(1.0)	21254.3154(0.0120)	-0.0054	34.771	34.062	} Ref. 3
10(1, 9) -	10(1,10)	25975.8300(1.0)	25975.8793(0.0152)	-0.0493	41.126	40.260	
11(1,10) -	11(1,11)		31168.7397(0.0206)		48.116	47.077	
12(1,11) -	12(1,12)		36832.5430(0.0287)		55.742	54.517	
13(1,12) -	13(1,13)		42966.8548(0.0404)		64.002	62.569	
14(1,13) -	14(1,14)		49571.1466(0.0563)		72.897	71.247	
15(1,14) -	15(1,15)		56644.7828(0.0770)		82.426	80.537	
16(1,15) -	16(1,16)		64187.0053(0.1033)		92.590	90.449	
10(2, 8) -	10(2, 9)		445.9878(0.0024)		59.206	59.191	
11(2, 9) -	11(2,10)		644.0204(0.0033)		66.116	66.094	
12(2,10) -	12(2,11)		901.3026(0.0044)		73.655	73.625	
13(2,11) -	13(2,12)		1228.4959(0.0056)		81.824	81.787	
14(2,12) -	14(2,13)		1637.0901(0.0069)		90.623	90.568	
15(2,13) -	15(2,14)		2139.3779(0.0083)		100.052	99.980	
16(2,14) -	16(2,15)		2748.4245(0.0097)		110.111	110.019	
17(2,15) -	17(2,16)		3478.0305(0.0111)		120.801	120.685	
18(2,16) -	18(2,17)		4342.6882(0.0122)		132.122	131.977	
19(2,17) -	19(2,18)		5357.5299(0.0131)		144.074	143.896	
20(2,18) -	20(2,19)		6538.2695(0.0135)		156.659	156.441	
21(2,19) -	21(2,20)	7901.0800(1.0)	7901.1348(0.0133)	-0.0548	169.875	169.612	Ref. 3
22(2,20) -	22(2,21)	9462.8040(1.0)	9462.7934(0.0125)	0.0106	183.725	183.439	
23(2,21) -	23(2,22)	11240.2820(1.0)	11240.2688(0.0111)	0.0132	198.207	197.832	
24(2,22) -	24(2,23)	13250.8640(1.0)	13250.8512(0.0101)	0.0128	213.323	212.881	
25(2,23) -	25(2,24)	15512.0090(1.0)	15511.9998(0.0121)	0.0092	229.073	228.556	
26(2,24) -	26(2,25)	18041.2330(1.0)	18041.2401(0.0191)	-0.0071	245.457	244.856	
27(2,25) -	27(2,26)	20855.9300(0.0)	20856.0572(0.0308)	-0.1272	262.476	261.790	Ref. 3
28(2,26) -	28(2,27)		23973.7848(0.0474)		280.130	279.330	
29(2,27) -	29(2,28)		27411.4936(0.0693)		298.419	297.505	

Tables VII and VIII show the variation of the derived parameters due to the different planarity conditions. These tables contain also the values of the quartic distortion constants $\hbar^4 \tau_{aabb}$, τ'_{bbcc}, τ'_{ccaa} and $\hbar^4 \tau_{abab}$ as calculated from normal-coordinate analysis [11].

The errors of the determinable and derived rotational parameters were estimated on the basis of standard errors of the spectroscopic constants obtained from the least-squares process and are given in Tables I and II. The calculation of these errors was done via numerical propagation of errors, and was also checked by variance propagation formulae using zero co-variance assumptions.

b) Discussion of Errors

The problem whether there are systematic errors present in the results of our calculations was examined using residual analysis. The residual errors of the least-squares calculations were first reduced to "unit normal deviate" form (see Draper-Smith [23]) by dividing the residuals by their estimated error:

$$s^2 = \sum_i^n e_i^2/(n-p)$$

where n is the number of residual error data, while $(n-p)$ is the excess degrees of freedom of transitions fitted over the number of parameters in the Hamiltonian. The statistics of such a distribution should approach those of a normal distribution with zero average and unit standard deviation, provided there are no systematic errors present. The results of such an analysis are more or less in accord with the assumption of normality in the error distribution. The values of the standard deviation and the mean of the "unit normal deviate" residuals of ketene-d_2 and ketene-d_1 are 0.9168 and -0.095, and 0.9554 and 0.0292, respectively.

Another test of residual correlations was made by examining the correlation among the residuals and the K_a values. This test yielded coefficients of determination $r^2 = 0.134$ and 0.012 for ketene-d_1 and ketene-d_2. A similar test of correlation among the residuals and their J values yielded coefficients of determination: $r^2 = 0.042$ and 0.003 for ketene-d_1 and ketene-d_2, respectively. These correlations are therefore insignificant.

As to the correlations found among constants obtained from the least-squares calculations, i. e. be-

tween the spectroscopic constants in Watson's reduced representation the following were noted. The strongest correlations exist between the members of the following groups (A, B, C), (A, δ_K), (B, δ_K), (C, δ_K) and (δ_K, δ_J), while no significant correlations were found for the two sextic constants. The correlations among the rotational constants A, B and C are due to the fact that these three constants were refined separately. The correlations between B and δ_K, furthermore between C and δ_K are analogous to the correlations found by Johns, Stone and Winnewisser [6] for ketene-h_2 between $(B-C)$ and δ_K. This correlation was also pointed out by Sheridan [10].

The results of the fitting procedure, the calculated and measured transitions, including some predicted transitions for ketene-d_2 and ketene-d_1 are found in Tables IX and X, respectively. As can be seen from the latter tables the standard error of prediction for both deuterated species is somewhat greater than for ketene-h_2 [6]. This is a consequence of the lack of high resolution infrared data on these molecular species.

Table XI. Comparison of inertial defect values in [amu·Å²] from different representations of spectroscopic constants with values from normal-coordinate analysis (Ref. [11]).

	Reduced repr. value	Average of derived const.	Normal-coord. value
CD_2CO	0.114457 (83)	0.11386 (10)	0.11522
CHDCO	0.10265 (30)	0.101993 (35)	0.10117

The results obtained in this paper may be used to support the planar model of ketene, as the inertial defect values calculated from normal-coordinate analysis compare favourably with the various experimental inertial defect values. Table XI contains such a comparison which yields a satisfactory agreement. A similar conclusion may be derived from the value of the τ defect for ketene-d_2, although this quantity is more difficult to assess than the inertial defect values, and its relative error is greater in this work. The value of the τ defect was found to be undetermined by the present data for ketene-d_1. The origin of the τ defect is also the reason for the differences among the derived constants in Tables VII and VIII; they contain vibrational contributions due to zero-point vibrations.

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