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Microwave Spectrum of Acetyl Iodide*

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The microwave spectra of CH_3COI and CD_3COI were investigated in the region 8000 to 27 000 Mc/sec. The effects of internal rotation and quadrupole perturbations were found to be essentially independent. The height of the potential barrier hindering the methyl group internal rotation was determined to be 1301 ± 30 cal/mole from measured CH_3COI doublet splittings. Level mixing was found for several pairs of rotational states, analogous to Fermi resonance in vibrational levels. Mixing effects permitted determination of the quadrupole coupling constant χ_{ab} in both isotopic species. The values for quadrupole coupling constants in CH_3COI are $\chi_{aa}=-1563\pm2$, $\chi_{bb}=914\pm2$, and $\chi_{ab}=-135.6\pm2$ Mc/sec. In CD_3COI the values are $\chi_{aa}=-1541\pm3$, $\chi_{bb}=892\pm2$, and $\chi_{ab}=-258.5\pm10$ Mc/sec. Diagonalization of each of the above tensors gives $\chi_{\alpha\alpha}=-1569$ and $\chi_{\beta\beta}=920$ Mc/sec.

I. INTRODUCTION

THIS work is part of a systematic study of molecules with the general formula CH_3COZ, the "acetyl" series.[1–3] A primary motive for work on this series is elucidation of the nature of the potential barrier which hinders internal rotation of the CH_3 group about the C–C axis.

The analysis of internal barrier effects in acetyl iodide proceeded in much the same way as for acetyl chloride[3] and acetyl bromide.[2] The height of the hindering barrier was found to be virtually the same in the iodide as in the chloride and bromide.

The quadrupole hyperfine effects were more complicated in the case of the iodide than for the other halides. While first-order perturbation theory was sufficient to account for hyperfine effects in the chloride and bromide, acetyl iodide hyperfine structure (hfs) required use of both first- and second-order perturbation theory. A computer program was written to generate the second-order corrections.

II. EXPERIMENTAL

Both CH_3COI and CD_3COI were prepared by the method of Thiele and Haakh.[4] A 3-g quantity of red phosphorous was added to 10 cc of acetic anhydride in a 500-cc three-neck flask. A reflux condenser and $CaCl_2$ drying tube were placed in the center neck of the flask. The other two necks were fitted for later addition of reagents.

The flask was heated for 1 h in a water bath with gradual addition of 28 g of iodine. Gelation occurred and the reflux condenser was replaced by a distilling column packed with glass helices. An additional 1.5 g of phosphorous was then added and the flask was heated for several minutes, after which the contents were distilled.

The CH_3COI was collected at 105°C and the CD_3COI at 103.5°C. The yield in each case was about 4 cc. The product was pale orange, and storage at room temperature rapidly turned it dark brown. Samples stored at dry ice temperature remained undecomposed for months.

The spectrometer used was a Stark-effect type with 100-kc/sec square-wave modulation. Frequency measurements were made with multiples of a 5-Mc/sec crystal oscillator, monitored by radio station WWV. Both oscilloscope and recorder display were used, and all runs were made with the Stark cell at dry ice temperature. Observations were made of *a*-type and *b*-type transitions of CH_3COI and CD_3COI in the frequency range 8000 to 27 000 Mc/sec.

III. OBSERVED SPECTRA

Observed transitions with detailed quadrupole and internal rotation assignments are listed in Tables I and II.

For $J>3$ R-branch transitions, the six strongest hyperfine components (the iodine nuclear spin of 5/2 gives rise to six F values when $J>3$) are described by the selection rule $\Delta F=1(F\rightarrow F+1)$. For Q branches involving J values of 4 or higher, the strong sextet is that involving the six $F\rightarrow F$ transitions.

The general transition thus appears as a sextet of hyperfine components, in the absence of resolved internal rotation structure. When both internal rotation and quadrupole perturbation components are fully resolved, 12 distinct lines may be observed for each rigid-rotor transition.

If the quadrupole and internal rotation effects were independent, the transitions would appear as sextets of doublets, with each doublet spacing the same. This was found to be the case for those CH_3COI transitions which were fully resolved.

Many additional intense high-J multiplets have been measured and assigned to the rigid rotator. Details of

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[1] L. C. Krisher and E. B. Wilson, Jr., J. Chem. Phys. **31**, 882 (1959).

[2] L. C. Krisher, J. Chem. Phys. **33**, 1237 (1960).

[3] K. M. Sinnott, J. Chem. Phys. **34**, 851 (1961).

[4] J. Thiele and H. Haakh, Ann. Chem. **369**, 145 (1909).

Table I. Observed spectra of CH_3COI.[a]

Transition	$F \rightarrow F'$	σ	ν_{obs} (Mc/sec)
a Type			
$5_{0,5}$–$6_{0,6}$	7/2–9/2	b	23 769.83
	5/2–7/2	b	23 776.65[c]
	9/2–11/2	b	23 777.45
	11/2–13/2	b	23 792.33
	15/2–17/2	b	23 795.52
	13/2–15/2	b	23 803.45
$5_{1,4}$–$6_{1,5}$	7/2–9/2	b	25 226.12
	9/2–11/2	b	25 227.88
	11/2–13/2 5/2–7/2	b b	25 239.91[c]
	13/2–15/2	b	25 253.32
	15/2–17/2	b	25 255.18
b Type			
$0_{0,0}$–$1_{1,1}$	5/2–3/2	b	11 839.75
	5/2–7/2	b	11 923.31
	5/2–5/2	b	12 117.86
$1_{0,1}$–$2_{1,2}$	3/2–5/2	b	15 368.50
	3/2–3/2	b	15 469.61
	7/2–7/2	b	15 482.72
	3/2–1/2	b	15 542.77
	7/2–9/2	b	15 600.22
	5/2–7/2	b	15 809.89
	5/2–5/2	b	15 839.47
	5/2–3/2	b	15 940.35
$2_{0,2}$–$3_{1,3}$	9/2–11/2	b	19 087.37
	5/2–7/2	b	19 115.06
	3/2–3/2	b	19 135.86
	7/2–9/2	b	19 201.36
$3_{1,2}$–$3_{2,1}$	11/2–11/2	b	23 192.91
	7/2–7/2 9/2–7/2	b b	23 427.22[c]
	9/2–11/2	b	23 428.84
	7/2–9/2	b	23 432.70[c]
	9/2–9/2	b	23 433.13[c]
$4_{1,3}$–$4_{2,2}$	3/2–3/2	b	22 555.29
	13/2–13/2	b	22 622.77
	5/2–5/2	b	22 640.50
	11/2–11/2	b	22 767.45
	9/2–9/2	b	22 781.23
$5_{0,5}$–$5_{1,4}$	11/2–11/2 9/2–9/2	*E* *E*	11 286.95[c]
	11/2–11/2	*A*	11 287.68[c]
	13/2–13/2 9/2–9/2	*E* *A*	11 288.02[c]
	7/2–7/2 13/2–13/2	*E* *A*	11 288.95
b Type			
$5_{0,5}$–$5_{1,4}$ (*Cont*)	7/2–7/2 15/2–15/2	*A* *E*	11 289.88
		A	11 290.82
	5/2–5/2	*E*	11 291.47[c]
		A	11 292.18[c]
$6_{1,6}$–$7_{0,7}$	11/2–13/2	b	22 685.10
	13/2–15/2	b	22 686.98
	9/2–11/2	b	22 697.10
	15/2–17/2	b	22 701.07
	7/2–9/2	b	22 723.66
	17/2–19/2	b	22 726.95
$7_{0,7}$–$7_{1,6}$	15/2–15/2	*E*	14 537.61
		A	14 539.07
	13/2–13/2	*E*	14 541.86
	17/2–17/2	*A* *E*	14 543.40
		A	14 544.96
	11/2–11/2	*E*	14 553.32
		A	14 554.77
	19/2–19/2	*E*	14 561.89
		A	14 563.35
	9/2–9/2	*E*	14 568.24
		A	14 569.72
$8_{0,8}$–$8_{1,7}$	17/2–17/2	*E*	16 722.45
		A	16 724.38
	15/2–15/2	*E*	16 727.32
		A	16 729.19
	19/2–19/2	*E*	16 730.54
		A	16 732.38
	13/2–13/2	*E*	16 741.48
		A	16 743.41
	21/2–21/2	*E*	16 753.30
		A	16 755.17
	11/2–11/2	*E*	16 760.95
		A	16 762.83
$10_{0,10}$–$10_{1,9}$	21/2–21/2	*E*	22 251.68
		A	22 254.64
	19/2–19/2	*E*	22 256.83
		A	22 259.82
	23/2–23/2	*E*	22 260.86
		A	22 263.75
	17/2–17/2	*E*	22 272.41
		A	22 275.39
	25/2–25/2	*E*	22 291.19
		A	22 294.20
	15/2–15/2	*E*	22 296.72
		A	22 299.70

[a] Estimated uncertainty ±0.15 Mc/sec unless otherwise stated. [b] Internal rotation (*A*–*E*) splittings not resolved. [c] Unresolved or poorly resolved line.

the hfs for these groups of lines have not been calculated and they are not reported in the tables.

IV. ROTATIONAL CONSTANTS

In order to determine the molecular rigid rotational constants *A*, *B*, *C*, the observed spectra must be corrected for quadrupole and internal rotation effects to determine the hypothetical "center" frequencies where rigid-rotor transitions would occur in the absence of these perturbations. Table III compares center frequencies derived from the data with those calculated from *A*, *B*, and *C*.

TABLE II. Observed spectra of CD_3COI.[a,b]

Transition	$F \rightarrow F'$	ν_{obs} (Mc/sec)
a-Type		
$5_{1,4}-6_{1,5}$	7/9–9/2	23 209.40
	9/2–11/2	23 212.41
	5/2–7/2	23 223.38
	11/2–13/2	23 224.91
	13/2–15/2	23 234.80
	15/2–17/2	23 240.02
$6_{0,6}-7_{0,7}$	9/2–11/2	25 278.16
	7/2–9/2	25 281.39
	11/2–13/2	25 284.60
	13/2–15/2 17/2–19/2	25 295.18
	15/2–17/2	25 301.64
b-Type		
$0_{0,0}-1_{1,1}$	5/2–3/2	10 221.32
	5/2–7/2	10 302.90
	5/2–5/2	10 493.10
$2_{0,2}-3_{1,3}$	3/2–5/2	16 780.80
	9/2–11/2	16 874.56
	5/2–7/2	16 895.84
	3/2–3/2	16 901.17
	7/2–9/2 7/2–7/2	16 979.28[c]
	5/2–5/2	16 994.09
$4_{0,4}-4_{1,3}$	13/2–13/2	8 736.89
	5/2–5/2	8 738.46
	7/2–7/2	8 746.73
	11/2–11/2 9/2–9/2	8 752.68[c]
$5_{1,5}-5_{2,4}$	5/2–5/2	23 074.53
	15/2–15/2	23 097.68
	9/2–9/2	23 147.22
	13/2–13/2	23 156.81
	11/2–11/2	23 166.01
$7_{1,6}-7_{2,5}$	9/2–9/2	17 293.64[c]
	19/2–19/2	17 306.31
	11/2–11/2	17 326.27
	17/2–17/2	17 350.38
	13/2–13/2	17 351.33
	15/2–15/2	17 362.27
b-Type		
$7_{2,6}-8_{1,7}$	15/2–17/2	15 090.77
	17/2–19/2	15 101.60
	13/2–15/2	15 105.30[c]
	11/2–13/2	15 136.36
	19/2–21/2	15 153.59
	9/2–11/2	15 175.23
$8_{0,8}-8_{1,7}$	15/2–15/2	15 077.64
	13/2–13/2	15 082.90
	17/2–17/2	15 084.82
	19/2–19/2	15 098.55
	11/2–11/2	15 101.60
	21/2–21/2	15 106.87
$10_{1,9}-10_{2,8}$	15/2–15/2	17 356.90
	25/2–25/2	17 358.81
	17/2–17/2	17 365.28
	23/2–23/2	17 369.69
	19/2–19/2	17 370.80
	21/2–21/2	17 372.85
$11_{0,11}-11_{1,10}$	23/2–23/2	23 481.11
	21/2–21/2	23 485.40
	25/2–25/2	23 490.28
	19/2–19/2	23 500.27
	27/2–27/2	23 518.43
	17/2–17/2	23 523.26
$28_{9,19}-27_{10,18}$ $28_{9,20}-27_{10,17}$	51/2–49/2 61/2–59/2	23 799.04[c] 23 800.25[c]
	53/2–51/2	23 821.55
	59/2–57/2	23 824.48
	55/2–53/2	23 834.00
	57/2–55/2	23 835.29
$28_{7,21}-29_{6,24}$	57/2–59/2 55/2–57/2	23 447.02[c]
	59/2–61/2	23 453.36
	53/2–55/2	23 454.60
	61/2–63/2 51/2–53/2	23 468.60[c]

[a] Estimated uncertainty ±0.15 Mc/sec unless otherwise indicated. [b] No internal rotor splittings were resolved. [c] Unresolved or poorly resolved line.

No internal rotation doublets were observed in the CD_3COI spectrum due to the increased I_α of the deuterated methyl group. Since the CD_3COI quadrupole and rigid-rotor problems could be solved without internal rotation complications, this species was analyzed first.

Preliminary analysis on the *Q*-branch spectrum of CH_3COI determined approximate values of $\frac{1}{2}(A-C)$ and $\kappa=(2B-A-C)/(A-C)$. It was then possible to find a rigid-rotor structure which fits these two parameters. This was done by using the "acetyl" structure determined by Sinnott[3] for acetyl chloride and adjusting the position of the iodine mass. This structure was used, replacing deuterium for normal hydrogen, to predict a spectrum for CD_3COI from which the *Q*-branch study of that species began.

After κ was established from the *Q*-branch lines, $\frac{1}{2}(A+C)$ was determined from *R*-branch transitions. Low-*J* transitions were used for the final determination of the constants listed in Table IV. The moments of inertia in this table were derived from the rotational constants using the conversion factor 505 531 amu·Å²·Mc/sec.

V. BARRIER TO INTERNAL ROTATION

The interaction of internal and over-all rotation produced observable doublets in certain high-*J* transi-

TABLE III. Experimental[a] and calculated[b] rigid-rotor transition frequencies in acetyl iodide (megacycles per second).

Transition	CH_3COI Experimental[a]	Calculated[b]	Transition	CD_3COI Experimental[a]	Calculated[b]
$0_{0,0}$–$1_{1,1}$	11 968.59	11 968.70	$0_{0,0}$–$1_{1,1}$	10 346.96	10 346.97
$1_{0,1}$–$2_{1,2}$	15 631.78	15 631.66	$2_{0,2}$–$3_{1,3}$	16 897.93	16 897.84
$2_{0,2}$–$3_{1,3}$	19 111.93	19 111.93	$4_{0,4}$–$4_{1,3}$	8 745.10	8 744.97
$3_{1,2}$–$3_{2,1}$	23 300.94	23 300.80	$5_{1,5,}$–$5_{2,4}$	23 129.60	23 129.72
$4_{1,3}$–$4_{2,2}$	22 695.89	22 695.86	$5_{1,4}$–$6_{1,5}$	23 230.21	23 230.10
$4_{0,4}$–$4_{1,3}$	10 154.58	10 154.52	$6_{0,6}$–$7_{0,7}$	25 292.96	25 292.91
$5_{0,5}$–$5_{1,4}$	11 289.17	11 289.06	$7_{1,6}$–$7_{2,5}$	17 333.36	17 333.70
$5_{0,5}$–$6_{0,6}$	23 791.40	23 791.33	$7_{2,6}$–$8_{1,7}$	15 125.94	15 125.58
$5_{1,4}$–$6_{1,5}$	25 245.13	25 244.94	$8_{0,8}$–$8_{1,7}$	15 092.97	15 093.00
$6_{1,6}$–$7_{0,7}$	22 705.57	22 705.31	$10_{1,9}$–$10_{2,8}$	17 365.79	17 366.56
$7_{0,7}$–$7_{1,6}$	14 550.79	14 550.67	$11_{0,11}$–$11_{1,10}$	23 499.81	23 500.99
$8_{0,8}$–$8_{1,7}$	16 738.85	16 738.77	$28_{9,19}$–$27_{10,18}$	23 819.13	23 827.02
$10_{0,10}$–$10_{1,9}$	22 272.61	22 272.97	$28_{9,20}$–$27_{10,17}$		23 827.16
			$28_{7,21}$–$29_{6,24}$	23 456.50	23 468.13

[a] Derived from observed spectra by correcting for hyperfine and internal rotation effects. [b] Calculated from rotational constants in Table IV.

tions of CH_3COI. The height of the barrier hindering internal rotation of the CH_3 group about the C–C axis was determined from measured doublet splittings using the theory of Kilb, Lin, and Wilson[5] and Herschbach.[6]

The theory assumes a potential-energy barrier of the form $V=\frac{1}{2}V_3(1-\cos 3\alpha)$, where α is the angle of internal rotation.

The "high-barrier approximation" is applicable to acetyl iodide, i.e., only second-order perturbations are observable. The perturbation effects give rise to slightly different effective, or pseudorigid, rotational constants for the two types of torsional levels. Transitions between the A (nondegenerate) and E (doubly degenerate) torsional levels are forbidden because the molecular dipole moment is independent of the internal rotation angle. The resulting spectrum is thus doublets of nearby A and E pseudorigid-rotor transitions.

TABLE IV. Rotational constants and moments of inertia.[a]

	CH_3COI	CD_3COI
A	10 137.22 Mc/sec	8 666.38
B	2 206.97	2 034.23
C	1 831.48	1 680.59
I_a	49.8688 amu·Å^2	58.3324
I_b	229.0611	248.5122
I_c	276.0232	300.8057

[a] Estimated uncertainty ±0.10 Mc/sec.

A particular doublet splitting can be written[7]

$$\nu_A-\nu_E=\Delta\nu_{J,\tau\rightarrow J',\tau'}$$
$$=\Delta A\frac{\partial\Delta E}{\partial A}+\Delta B\frac{\partial\Delta E}{\partial B}+\Delta C\frac{\partial\Delta E}{\partial C},$$

where $\Delta E=E_{J',\tau'}-E_{J,\tau}$ is the rigid-rotor transition frequency and $\Delta A=\Delta W^{(2)}(I_\alpha{}^2\lambda_a{}^2/I_a{}^2)F$. For acetyl iodide this becomes

$$\Delta\nu_{J,\tau\rightarrow J',\tau'}=I_\alpha{}^2F\Delta W^{(2)}\left(\frac{\lambda_a{}^2}{I_a{}^2}\frac{\partial}{\partial A}\Delta E+\frac{\lambda_b{}^2}{I_b{}^2}\frac{\partial}{\partial B}\Delta E\right).$$

The quantity $\Delta W^{(2)}$ is tabulated[8] in terms of a parameter s which is related to the barrier height by

$$V_3=\tfrac{9}{4}Fs.$$

The notation is that of Ref. 6.

This set of relations determines V_3 for the measured $\nu_A-\nu_E$, with given values for the structural parameters λ_a, λ_b, and I_α. If acetyl iodide were a classical rigid body, it would be true that

$$I_\alpha=I_a+I_b-I_c.$$

Since vibration and rotation are not separable, this relation is not exact for the moments of inertia derived from microwave data. An "inertial defect"[9] must be added to the right-hand side when the I's in Table IV are used. A reasonable value of the inertial defect for the acetyl series is[2] 0.2 amu·Å^2 and gives $I_\alpha=3.11$

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[5] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys. **26**, 1695 (1957).

[6] D. R. Herschbach, J. Chem. Phys. **31**, 91 (1959).

[7] J. D. Swalen and D. R. Herschbach, J. Chem. Phys. **27**, 100 (1957).

[8] Reference 6, Appendix C.

[9] V. W. Laurie, J. Chem. Phys. **28**, 704 (1958).

amu·Å^2 for acetyl iodide. This is close to the conventional value of 3.14 amu·Å^2 which was used in the V_3 calculation. The barrier height is sensitive to I_α. The I_α value is not precisely known, however, because of this inertial defect which gives rise to the major uncertainty in V_3. The assumed structural constants are uncertain also, but their effect on V_3 is less direct. The structural values in Table V are based on the CH_3CO structure from acetyl chloride,[3] with an iodine position adjusted to fit the rotational constants in Table IV.

VI. QUADRUPOLE COUPLING CONSTANTS

The energies associated with the quadrupole moment of the iodine nucleus required the use of second-order perturbation theory to obtain accurate hfs predictions. The diagonal quadrupole coupling constants[10] $\chi_{gg}=eQ(\partial^2V/\partial g^2)$ (where $g=a$, b, c, the molecule principal axes), were obtained graphically after correcting the observed spectra for second-order effects.

Two computer programs were used to calculate the second-order quadrupole corrections. One of them used the matrix elements of Van Vleck,[11] and the other employed those of Bragg,[12] and King, Hainer, and Cross.[13] After adjustment for phase differences in the two schemes, the programs agreed to better than 0.01 Mc/sec for all predictions.

There were several pairs of levels, however, for which these perturbation techniques gave incorrect results: ($1_{1,0}$ and $2_{0,2}$) in CH_3COI; ($1_{1,0}$ and $2_{0,2}$), ($4_{2,2}$ and $5_{1,4}$), and ($7_{2,6}$ and $8_{0,8}$) in CD_3COI. These pairs of levels were all less than 600 Mc/sec apart and $c_{12}^{(1)}=V_{21}/(E_1^0-E_2^0)$, where V_{21} is a matrix element of the quadrupole Hamiltonian, was found to be large, due to the small energy denominator, so that some modification was required. A perturbed wavefunction was written

$$\psi_1=a_1\psi_1^0+b_1\psi_2^0+\sum_{m;m\neq1,2}c_{1m}\psi_m^0,$$

where a_1, b_1 are zero order in the smallness parameter λ, and $c_{1m}=\lambda c_{1m}^{(1)}+\lambda^2c_{1m}^{(2)}+\cdots(m\neq1,2)$. The time-independent Schrödinger equation then became

$$(H^0+\lambda V)(a_1\psi_1^0+b^1\psi_2^0+\sum_{m;m\neq1,2}C_{1m}\psi_m^0)$$
$$=E_1(a_1\psi_1^0+b_1\psi_2^0+\sum_{m;m\neq1,2}C_{1m}\psi_m^0),$$

where $E_1=E_1^0+\lambda E_1^{(1)}+\lambda^2E_1^{(2)}+\cdots$. This equation was solved to first order in λ for the constants a_1 and b_1, the constants being determined from the pair of homogeneous equations, $a_1(W_{11}-\mathcal{E})+b_1V_{12}=0$ and $a_1V_{21}+b_1(W_{22}-\mathcal{E})=0$, where $\mathcal{E}=E_1^0+\lambda E_1^{(1)}$. These equations lead to the same secular equation for $\mathcal{E}$ as is found for the eigenvalues when $\psi_\pm=a^\pm\psi_1^0+b_\pm\psi_2^0$ are sought as eigenfunctions of the total Hamiltonian. The mixed energies have the usual 2×2 form

$$E_\pm=\tfrac{1}{2}(W_{11}+W_{22})\pm[\tfrac{1}{2}(W_{11}-W_{22})^2+|W_{12}|^2]^{\frac{1}{2}},$$

where

$$W_{\alpha\beta}=\int d\tau\psi_\alpha^*(H^0+\lambda V)\psi_\beta.$$

A simple way to utilize the usual perturbation formulas is to then use $\psi_\pm$ instead of ψ_1^0 and ψ_2^0 in the set of basis functions. Since the effect of $(H^0+\lambda V)$ on $\psi_\pm$ is known, one may define $H_{++}^0=E_+$, $H_{--}^0=E_-$, and $V_{++}=V_{--}=V_{+-}=V_{-+}=0$. This formally treats V as part of the unperturbed Hamiltonian for mixed level matrix elements. Now, the standard perturbation results apply, with all other matrix elements defined in the usual way.

The second-order correction to a mixed level becomes

$$E_\pm^{(2)}=|a_\pm|^2E_1^{(2)}+|b_\pm|^2E_2^{(2)}$$
$$+2\,\mathrm{Re}a_\pm^*b_\pm\sum_{k;k\neq1,2}\frac{V_{1k}V_{k2}}{E_\pm-E^{k0}}.$$

These mixed level second-order corrections were found to be noticeably different from unmixed level corrections in some low-J levels, or where large mixing occurred. The cross term is always real, and in a few cases was 0.1 or 0.2 Mc/sec in size. It might be thought that the cross terms could be used to determine the sign of χ_{ab}, but all terms, including cross terms, depend on the square of χ_{ab}.

As a check on the modified theory, one should observe that this correction goes over to the usual unmixed form as the energy separation of the mixed pair increases. If $W_{11}>W_{22}$, as the levels separate, $|a_+|^2\rightarrow1$

TABLE V. Internal barrier and assumed structural constants.

F	1.64841×10^5 Mc/sec
λ_a	0.44177
λ_b	0.89713
I_α	3.14 amu·Å^2
V_3 from $7_{0,7}$–$7_{1,6}$	1305 cal/mole
V_3 from $8_{0,8}$–$8_{1,7}$	1301
V_3 from $10_{0,10}$–$10_{1,9}$	1296
V_3	1301±30

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[10] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., Inc., New York, 1955), Chap. 6.

[11] J. H. Van Vleck, Rev. Mod. Phys. **23**, 213 (1951).

[12] J. K. Bragg, Phys. Rev. **74**, 533 (1948).

[13] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944).

and $|b_+|^2 \rightarrow 0$, so we find

$$E_+^{(2)} \rightarrow \sum_{n;n\neq 1,2} \frac{|V_{1n}|^2}{E_1^0+V_{11}-E_n^0}$$

$$\simeq \sum_{n;n\neq 1,2} \frac{|V_{1n}|^2}{E_1^0-E_n^0} - V_{11} \sum_{n;n\neq 1,2} \frac{|V_{1n}|^2}{(E_1^0-E_n^0)^2}.$$

The last term is third order in smallness and is essentially that which disappears from the $E_+^{(3)}$ expression when V_{++} is formally set to zero. The $|V_{12}|^2/(E_1^0-E_2^0)$ term, missing above, occurs in the expanded square root of E_+.

Another effect investigated was the extent to which the mixing of two levels affected any third level. All cases of interest were such that the approximation

$$(E_1^0+V_{11}-E_n^0)^{-1} \simeq (E_1^0-E_n^0)^{-1} \times \{1-[V_{11}/(E_1^0-E_n^0)]\}$$

was valid. It was found that mixing at such energy separations produced small third-order effects, and it was sufficient to consider only the second-order effects produced by the unmixed levels.

Normally, the second-order perturbation of nearby levels produced a repulsion between them, i.e., a perturbation which couples them will mix the levels, and increase the energy separation between them, if one disregards perturbation effects of other levels on the pair. If the unperturbed levels are separated by less than a typical first-order perturbation energy, it is possible for the quadrupole perturbation to "invert" the ordering of levels. When $H^0_{11} > H^0_{22}$, but $(H^0_{11}+V_{11}) < (H^0_{22}+V_{22})$, the modified theory predicts that ψ_+ will be dominated by ψ^0_2, $(|a_+/b_+|^2 \ll 1)$ instead of by ψ^0_1 as would "normally" be expected.

The $7_{2,6}$ and $8_{0,8}$ levels in CD3COI offered an example of this behavior. The $8_{0,8}$ unperturbed rigid-rotor level is about 33 Mc/sec higher than the unperturbed $7_{2,6}$ level. Addition of first-order quadrupole energies to these levels placed the $7_{2,6}$ state higher for $F=17/2$ and $F=19/2$ and leaves the $8_{0,8}$ level higher for the 11/2, 13/2, and 15/2 F values. Measurement of the $7_{2,6}-8_{1,7}$ and $8_{0,8}-8_{1,7}$ transitions near 15 000 Mc/sec permitted a check of the theory. It also provided a good value for the unperturbed energy separation, which was iterated into the calculations as the hyperfine analysis progressed. Predictions based on the above theory agreed with the measured lines to experimental accuracy.

This form of perturbation theory correctly predicted the hfs of all transitions involving one level of a mixed pair. As a result, the value of χ_{ab} for each isotopic species was determined. In the absence of level mixing, energies associated with χ_{ab} are so small that no precise determination of its value can be made.

The signs of the diagonal χ's were determined from first-order theory. The χ_{ab} sign was inferred from the probable geometry of the molecule and the change in principal-axis systems for a CH_3 to CD_3 methyl-group substitution, assuming the χ tensor to be diagonal along the C–I bond.

When χ_{aa}, χ_{bb}, and χ_{ab} are determined, one may then make the transformation

$$R\begin{pmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ba} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{pmatrix} = \begin{pmatrix} \chi_{\alpha\alpha} & 0 & 0 \\ 0 & \chi_{\beta\beta} & 0 \\ 0 & 0 & \chi_{\gamma\gamma}=\chi_{cc} \end{pmatrix},$$

where R is a rotation matrix. This requires no structural assumptions, and we have explicitly

$$\left.\begin{matrix}\chi_{\alpha\alpha} \\ \\ \chi_{\beta\beta}\end{matrix}\right\} = \tfrac{1}{2}(\chi_{aa}+\chi_{bb}) \mp [\tfrac{1}{2}(\chi_{aa}-\chi_{bb})^2 + |\chi_{ab}|^2]^{\frac{1}{2}}.$$

The quadrupole coupling constants for CD_3COI and CH_3COI in both systems are given in Table VI.

At low J, some third-order quadrupole effects were observable. Exact calculations were not undertaken, except for the $0_{0,0}$ level, but inclusion of approximate third-order corrections definitely improved the hyperfine analysis, as Table VII indicates.

VII. DISCUSSION

The assumed iodine position which fit the rotational constants to a few megacycles per second involved a C–I distance of about 2.19 Å, and a CCI angle of 113°. This distance is longer than would be predicted from pure single bonding, and suggests ionic character in the bond, in addition to whatever double bonding may exist. Nothing more concrete can be stated, because the limited isotopic data in no way determined the iodine position, and because models like those discussed in Ref. 14 have not had complete success in correlating molecular properties.[15]

In acetyl iodide, the angle θ in the rotation matrix R is given by

$$\tan 2\theta = 2\chi_{ab}/(\chi_{aa}-\chi_{bb}).$$

If the χ tensor is diagonal along the C–I bond, this value of θ should agree with the angle between the

TABLE VI. Quadrupole coupling constants.

	CH_3COI (Mc/sec)	CD_3COI (Mc/sec)
χ_{aa}	-1563 ± 2	-1541 ± 3
χ_{bb}	914 ± 2	892 ± 2
χ_{cc}	649 ± 2	649 ± 2
χ_{ab}	-135.6 ± 2	-258.5 ± 10
$\chi_{\alpha\alpha}$	-1570	-1568
$\chi_{\beta\beta}$	921	919
$\chi_{\gamma\gamma}$	649	649

$\eta_{\mathrm{bond}} = -0.173$

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[14] Reference 10, Chap. 9.

[15] L. C. Krisher, thesis, Harvard University, Cambridge, Mass., 1959.

TABLE VII. Calculated and observed hfs in CH_3COI transition $1_{0,1}\rightarrow 2_{1,2}$ (megacycles per second).[a]

$F\rightarrow F'$	1^0	2^0	$3^{0\,b}$	ν_{calc}	ν_{obs}
$\frac{3}{2}-\frac{5}{2}$	-265.19	$+1.85$	$+0.08$	15 368.59	15 368.50
$\frac{3}{2}-\frac{3}{2}$	-172.48	$+10.46$	-0.21	15 469.62	15 469.61
$\frac{7}{2}-\frac{7}{2}$	-156.96	$+7.79$	$+0.08$	15 482.76	15 482.72
$\frac{3}{2}-\frac{1}{2}$	-89.03	$+0.01$	$+0.01$	15 542.84	15 542.77
$\frac{7}{2}-\frac{9}{2}$	-31.80	$+0.07$	$+0.01$	15 600.13	15 600.22
$\frac{5}{2}-\frac{7}{2}$	171.29	$+6.84$	$+0.01$	15 809.99	15 809.89
$\frac{5}{2}-\frac{5}{2}$	203.74	$+3.73$	$+0.05$	15 839.37	15 839.47
$\frac{5}{2}-\frac{3}{2}$	296.45	$+12.34$	-0.24	15 940.40	15 940.35

Hypothetical center 15 631.85[c]

[a] A–E splittings not resolved. [b] Approximate calculations. [c] Not corrected for internal rotation effects.

a axis and the C–I bond direction. In each isotopic species, the agreement between angles was better than 1°, using the assumed structure mentioned above. A related result is that the bond system χ's given in Table VI, calculated without recourse to an assumed structure, are in good agreement.

Lack of cylindrical symmetry in the electric-field gradient about the C–I bond is taken as a manifestation of double-bond character.[16] The contribution of a double-bonded structure[14] may be discussed in terms of

$$\eta_{\text{bond}}=(\chi_{\beta\beta}-\chi_{\gamma\gamma})/\chi_{\alpha\alpha}$$

or Goldstein's quantity[16]

$$\delta=(\chi_{\beta\beta}-\chi_{\gamma\gamma})/-\tfrac{3}{2}(eqQ)_{\text{atomic}}.$$

Howe and Goldstein[17] noted that the halogens could be ranked in the order Cl, Br, I with regard to their capacities for double bonding. This was done by comparing δ values in vinyl halides, and it was further noted that Ingold[18] had made the same ranking on the basis of chemical evidence. Data on the acetyl halides, Table VIII, show that the order of acetyl halide δ values agrees with the order given above. Comparison of η_{bond} values in the acetyl halides gives the same qualitative result.

TABLE VIII. Values of δ for acetyl and vinyl halides.

Z	CH_3COZ	C_2H_3Z
$^{35}Cl^{a}$	0.093[d]	0.06[f]
$^{79}Br^{b}$	0.085[e]	0.04[g]
I^{c}	0.079	0.03[f]

[a] Using $(eqQ)_{\text{atomic}}=-109.7$ Mc/sec, V. Jaccarino, and J. G. King, Phys. Rev. **83,** 471 (1951).

[b] Using $(eqQ)_{\text{atomic}}=770$ Mc/sec, J. G. King and V. Jaccarino, Phys. Rev. **94,** 1610 (1954).

[c] Using $(eqQ)_{\text{atomic}}=-2293$ Mc/sec, V. Jaccarino, J. G. King, R. A. Satten, and H. H. Stroke, **94,** 1798 (1954).

[d] Reference 3.

[e] Reference 2.

[f] Reference 16.

[g] C. D. Cornwell, J. Chem. Phys. **18,** 1118 (1950); see also Ref. 17.

Table VIII also shows acetyl C–Z bonds to possess roughly twice the double-bond character of C–Z bonds in the vinyl halides. This comparison is interesting[2] since each type of molecule has a pi-electron system adjacent to the C–Z bond, in the first case "carbonyl," in the second ethylenic.

The value determined for the internal barrier in acetyl iodide is virtually identical with those determined for acetyl bromide[2] and acetyl chloride.[3] This intensifies the already imposing evidence in support of Wilson's[19] statement that the barriers do not arise primarily from either steric repulsions or electrostatic interactions.

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[18] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, N.Y., 1953), p. 75.

[19] E. B. Wilson, Jr., Proc. Natl. Acad. Sci. U.S. **43,** 811 (1957).