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Analysis of Two Infrared Bands of CH_2D_2*

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Two infrared absorption bands of CH_2D_2 have been analyzed in the semirigid rotor approximation. These are the A-type band at 2671.67 cm^{-1} and the C-type band at 4425.61 cm^{-1}. The A-type band has previously been assigned as $\nu_3+\nu_9$, and the C-type band is tentatively assigned as $\nu_3+\nu_6$. The upper state of the A-type band is perturbed presumably by the close lying level $2\nu_5$. This interaction has not been investigated. The following values were found for the rotational constants of the ground vibrational state: $A_0=4.303$ cm^{-1}, $B_0=3.504$ cm^{-1}, $C_0=3.049$ cm^{-1}.

1. Introduction

The rotational-vibrational spectra of all the deuterated species of methane except CH_2D_2 have been well investigated [1].[1]

Methane and CD_4 are spherical tops while CH_3D and CD_3H are symmetric rotors; on the other hand CH_2D_2 is an asymmetric rotor. It seemed of interest to determine the rotational constants of CH_2D_2 in order to have a set of constants for each of the species. Fortunately, high resolution spectra could be obtained for both an A-type and a C-type band for this molecule. As recently discussed [2], this is sufficient data to enable a good determination of the ground state constants using the complementary $\Delta F_2''$ values obtained from the two bands. These two bands have been analyzed in the semirigid approximation to yield good values of the ground state constants. Unfortunately a perturbation in the excited state of the A-type band introduces an uncertainty in the effective constants for this band that is larger than can be justified for the precision of the data. Only transitions involving levels with low values of the rotational quantum numbers have been used in the analysis in order to minimize the effect of centrifugal distortion.

2. Experimental Procedure

The spectra were recorded with the grating instrument of the Infrared Spectroscopy Section [3] using a 10,000 lines/in. grating with a ruled area of about 6×8 in. A cooled PbS photoconductive cell was used as the detector.

Both the A- and C-type bands were recorded using a multiple reflection cell with a total path length of 6 m, filled with CH_2D_2 to a pressure of 2 cm of Hg. The C-type band was observed in the second order of the grating and the A-type band in the first. The CH_2D_2 obtained from Merck & Co., Ltd., had a stated minimum purity of 98%.

The wavelengths of the lines were measured using higher order infrared emission lines of the rare gases as standards, and interpolating between them through the use of the fringes of a Fabry-Perot interferometer as previously described [4].

3. Theory

Preliminary to the actual analysis of the spectra the mean square values of the angular momenta about the three principal axes of inertia and the intensities were calculated.

Assuming tetrahedral geometry and identical bond lengths of 1.094 A for CH_2D_2 the moments of inertia, reciprocal moments in cm^{-1} units, and the asymmetry parameter κ were obtained.

For the calculated value of $\kappa=-0.27$, α, β, and γ, as defined by Allen [2], were obtained by linear interpolation in published tables [5] of $E(\kappa)$ for each energy level.

α, β, and γ may be shown to be identical with $\langle P_z^2\rangle$, $\langle P_x^2\rangle$, and $\langle P_y^2\rangle$, respectively, in an I^r representation [6]. The energy of a rotational level in a given vibrational state, neglecting centrifugal distortion, may be written as [2]:

$$E(J_{K_{-1},K_1})=\alpha A_v+\beta B_v+\gamma C_v,$$

and the difference between two rotational levels in the same vibrational state as:

$$\Delta F=\Delta\alpha A_v+\Delta\beta B_v+\Delta\gamma C_v.$$

The $\Delta\alpha$'s, $\Delta\beta$'s and $\Delta\gamma$'s for each of the ΔF_2's observable from strong transitions in the A- and C-type band were calculated.

The strong transitions for the A-type band are those which satisfy the selection rules:

$$\Delta J=0,\ \pm1 \qquad \Delta K_{-1}=0 \qquad \Delta K_1=\pm1,$$

and for the C-type band the strong transitions are those for which

$$\Delta J=0,\ \pm1 \qquad \Delta K_{-1}=\pm1 \qquad \Delta K_1=0.$$

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[1] Figures in brackets indicate the literature references at the end of this paper.

The relative intensities of the transitions were calculated by combining the Boltzmann factor, calculated using the estimated moments of inertia, and nuclear spin statistics with the appropriate line strengths from published tables [7].

The nuclear spins of the equivalent pairs of hydrogen and deuterium atoms in CH_2D_2 give rise to degeneracies of the rotational levels. For the ground vibrational state the statistical weight factors are 15 for the symmetric (A) rotational levels and 21 for the antisymmetric (B) levels.

The A-type band at 2672 cm^{-1} has been previously observed by Wilmshurst and Bernstein [8] who assigned it to the combination $\nu_3+\nu_9$. As the observed band type is consistent with this assignment and there should be no other bands of this type near 2670 cm^{-1}, there appears to be no reason to doubt the assignment.

The C-type band at 4425 cm^{-1} can best be assigned at $\nu_3+\nu_6$ as this seems to be the only combination which would give a C-type band in the region 4400–4500 cm^{-1}.

4. Analysis

As each of the bands was isolated from others of comparable intensity, initial assignments, with the aid of the calculated intensities, could be made by inspection. From the initial assignments ΔF_2 values were obtained, and with the calculated $\Delta\alpha$'s, $\Delta\beta$'s, and $\Delta\gamma$'s were used to refine the values of A, B, and C in the ground and upper vibrational states. From these values of A, B, and C, α's, β's, and γ's pertinent to the value of κ in each vibrational state were calculated as before.

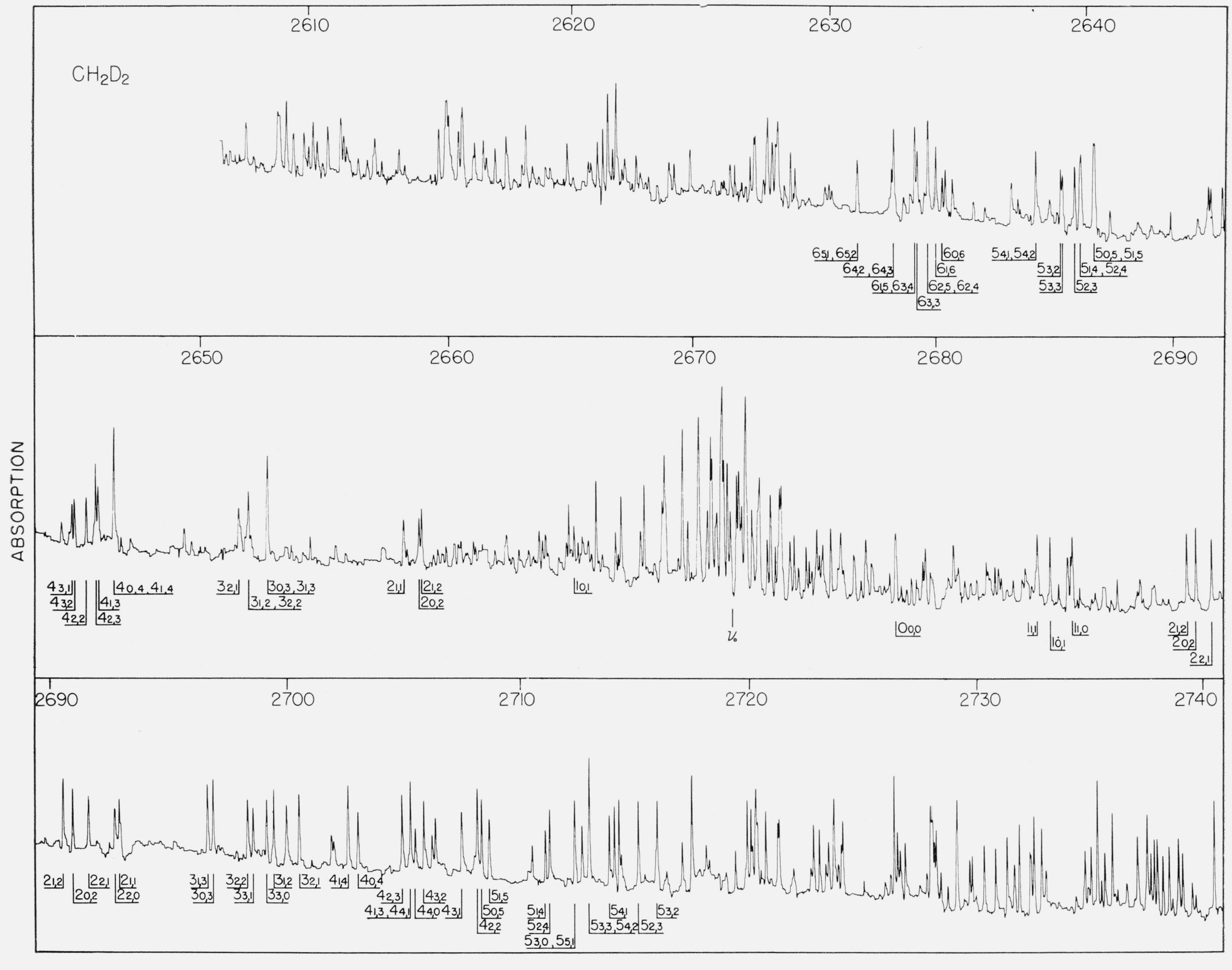

FIGURE 1. *The A-type band of* CH_2D_2 *at 2672 cm*$^{-1}$*.*

The identification given is the ground state designation of J_{K_{-1},K_1} for $R_{0,1}$ transitions to the high wave number side of the band origin, and for $P_{0,\bar{1}}$ transitions to the low wave number side of the band origin.

A trial spectrum was then calculated from the expression:

$$\nu=\nu_0+\alpha' A_v+\beta' B_v+\gamma' C_v-\alpha A_0-\beta B_0-\gamma C_0.$$

From the trial spectrum and intensities more transitions could be assigned, enabling further refinement of the reciprocal moments of inertia.

While this iterative procedure worked well with the C-type band, Coriolis perturbations in the A-type band caused some difficulty in definitely locating some of the transitions.

The lowest observably perturbed level in the $\nu_3+\nu_9$ vibrational state is the 4_{13} level which is pushed down by 0.24 cm^{-1}. For $J=5$, the levels 5_{05}, 5_{14}, and 5_{23} are all perturbed, and for $J=6$ over half of the levels are perturbed.

This perturbation has not been investigated in detail. It probably arises through interaction with the vibrational state $2\nu_5$, the fundamental of which is theoretically inactive in the infrared, but appears to have been observed at 1329 cm^{-1} [8], the transitions becoming allowed through Coriolis perturbation. ν_5 has apparently been observed in the Raman also at 1333 cm^{-1} [9].

No account was taken of the effect of centrifugal distortion in this analysis. Since only levels with low J values were used in the analysis, the effect of this correction on the rotational constants was minimized. No systematic differences between the observed and calculated spectra were noticed until rather high J values were reached. In these regions of the absorption serious overlapping of transitions make the unique assignment of transitions to observed absorption peaks doubtful.

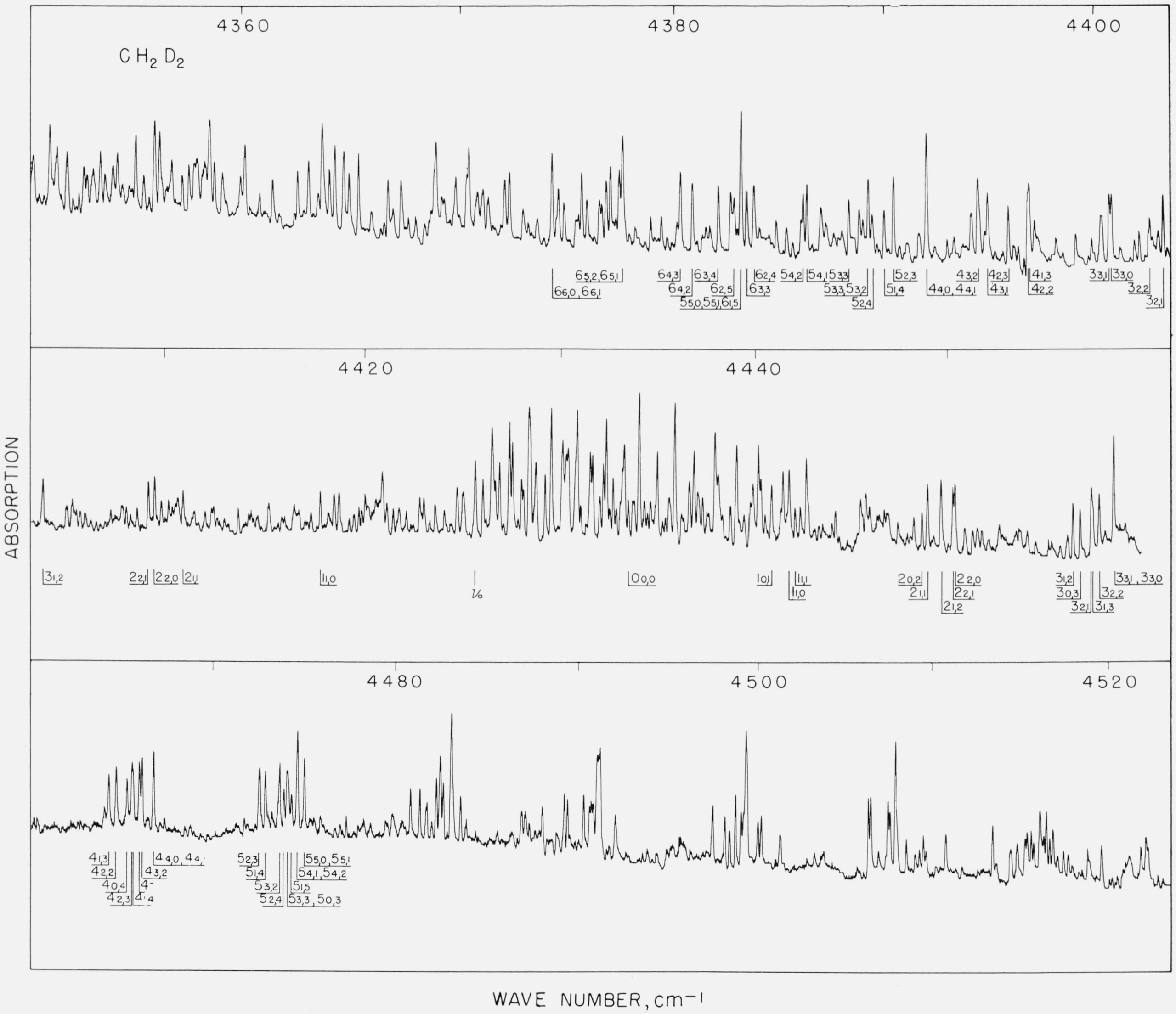

FIGURE 2. *The C-type band of* CH_2D_2 *at 4426 cm*$^{-1}$.

The identification given is the ground state designation of J_{K_{-1},K_1} for $R_{1,0}$ transitions to the high wave number side of the band origin, and for $P_{\bar{1},0}$ transitions to the low wave number side of the band origin.

Although no statistical analysis of the data was made, the excellent agreement between the observed and calculated ΔF_2 values for the ground state, and the sensitivity of the calculated ΔF_2 values to values of the rotational constants seem to indicate a probable error of the order of ± 0.002 cm^{-1} for each of the ground state constants. The agreement between the calculated and observed values of ΔF_2 for the ground state may be seen in table 1.

TABLE 1. *Ground state* $\Delta F_2''$

A-type band			C-type band		
$\Delta F_2''$	Calculated	Observed	$\Delta F_2''$	Calculated	Observed
	cm^{-1}	*cm*$^{-1}$		*cm*$^{-1}$	*cm*$^{-1}$
$0_{00}-2_{02}$	19.513	19.55	$0_{00}-2_{20}$	23.911	23.92
$1_{01}-3_{03}$	32.103	32.10	$1_{01}-3_{21}$	37.524	37.53
$1_{11}-3_{13}$	31.547	31.55	$1_{11}-3_{31}$	41.285	41.29
$1_{10}-3_{12}$	33.791	33.79	$1_{10}-3_{30}$	40.862	40.88
$2_{02}-4_{04}$	44.373	44.38	$2_{02}-4_{22}$	51.644	51.64
$2_{12}-4_{14}$	43.976	43.98	$2_{12}-4_{32}$	55.068	55.06
$2_{11}-4_{13}$	46.958	46.96	$2_{11}-4_{31}$	53.908	53.91
$2_{21}-4_{23}$	45.754	45.76	$2_{21}-4_{41}$	58.305	58.27
$2_{20}-4_{22}$	47.277	47.25	$2_{20}-4_{40}$	58.165	58.16
$3_{03}-5_{05}$	56.501	56.50	$3_{03}-5_{23}$	66.378	66.37
$3_{13}-5_{15}$	56.300	56.28	$3_{13}-5_{33}$	69.201	69.20
$3_{12}-5_{14}$	59.715	59.69	$3_{12}-5_{32}$	67.212	69.23
$3_{22}-5_{24}$	58.539	58.54	$3_{22}-5_{42}$	71.733	71.73
$3_{21}-5_{23}$	60.967	60.96	$3_{21}-5_{41}$	71.127	71.12
$3_{31}-5_{33}$	59.463	59.47	$3_{31}-5_{51}$	75.463	75.43
$3_{30}-5_{32}$	60.141	60.13	$3_{30}-5_{50}$	75.431	75.43
$4_{04}-6_{06}$	68.637	68.61	$4_{04}-6_{24}$	81.651	81.64
$4_{14}-6_{16}$	68.559	68.53	$4_{14}-6_{34}$	83.676	83.63
$4_{13}-6_{15}$	72.042	71.98	$4_{13}-6_{33}$	81.042	81.03
$4_{23}-6_{25}$	71,147	71.11	$4_{23}-6_{43}$	85.399	85.38
$4_{22}-6_{24}$	74.350	74.33	$4_{22}-6_{42}$	83.950	83.93
$4_{32}-6_{34}$	72.585	72.55	$4_{32}-6_{52}$	88.728	88.65
$4_{31}-6_{33}$	74.092	74.07	$4_{31}-6_{51}$	88.532	88.52
$4_{41}-6_{43}$	72.848	72.81	$4_{41}-6_{61}$	92.665	92.56
$4_{40}-6_{42}$	73.062	73.02	$4_{40}-6_{60}$	92.660	92.56

TABLE 2. *C-type band* $\Delta F_2'$

A=4.255 cm^{-1} B=3.590 cm^{-1} C=3.151 cm^{-1}

$\Delta F'_2$	Calc	Obs
	cm^{-1}	*cm*$^{-1}$
$0_{00}-2_{20}$	23.918	23.96
$1_{01}-3_{21}$	37.927	37.94
$1_{11}-3_{31}$	41.086	41.12
$1_{10}-3_{30}$	40.685	40.70
$2_{02}-4_{22}$	52.436	52.44
$2_{12}-4_{32}$	55.238	55.25
$2_{11}-4_{31}$	54.163	54.18
$2_{21}-4_{41}$	57.925	57.91
$2_{20}-4_{40}$	57.778	57.80
$3_{03}-5_{23}$	67.521	67.51
$3_{13}-5_{33}$	69.726	69.74
$3_{12}-5_{32}$	67.944	67.93
$3_{22}-5_{42}$	71.753	71.74
$3_{21}-5_{41}$	71.131	71.15
$3_{31}-5_{51}$	74.891	74.82
$3_{30}-5_{50}$	74.854	74.82
$4_{04}-6_{24}$	83.064	82.95
$4_{14}-6_{34}$	84.534	84.48
$4_{13}-6_{33}$	82.268	82.15
$4_{23}-6_{43}$	85.784	85.82
$4_{22}-6_{42}$	84.431	84.42
$4_{32}-6_{52}$	88.552	88.51
$4_{31}-6_{51}$	88.324	88.32
$4_{41}-6_{61}$	91.899	91.83
$4_{40}-6_{60}$	91.890	91.83

The constants for the excited states of these bands cannot be determined as precisely as those for the ground state with the available ΔF_2 values, but ± 0.005 cm^{-1} would seem to be a generous estimate of the probable error in the constants for these states. The calculated and observed ΔF_2 values for the excited states are compared in tables 2 and 3.

The constants determined for the three vibrational levels are given in table 4. The band origins were determined from the best fit between the observed and calculated spectra for low J values.

TABLE 3. *A-type band* $\Delta F_2'$

A=4.254 cm^{-1} B=3.654 cm^{-1} C=3.019 cm^{-1}

$\Delta F_2'$	Calc	Obs
	cm^{-1}	*cm*$^{-1}$
$0_{00}-2_{02}$	19.715	19.70
$1_{01}-3_{03}$	33.132	32.11
$1_{11}-3_{13}$	31.617	31.62
$1_{10}-3_{12}$	34.688	34.68
$2_{02}-4_{04}$	44.163	44.17
$2_{12}-4_{14}$	43.916	43.91
$2_{11}-4_{13}$[a]	47.748	47.51
$2_{21}-4_{23}$	46.516	46.54
$2_{20}-4_{22}$	48.979	48.96
$3_{03}-5_{05}$[a]	56.159	56.51
$3_{13}-5_{15}$	56.080	56.07
$3_{12}-5_{14}$[a]	60.078	59.35
$3_{22}-5_{24}$	59.144	59.11
$3_{21}-5_{23}$[a]	62.809	62.70
$3_{31}-5_{33}$	60.862	60.86
$3_{30}-5_{32}$	62.271	62.59

[a] Perturbed levels.

TABLE 4. *Rotational and vibrational constants*

	Ground state	$\nu_3+\nu_9$	$\nu_3+\nu_6$
	cm^{-1}	*cm*$^{-1}$	*cm*$^{-1}$
A	4.303	4.254	4.255
B	3.504	3.654	3.590
C	3.049	3.019	3.151
ν_0	-----	2671.67	4425.61

5. References

[1] Among the more recent high resolution analyses are those of:
K. T. Hecht, J. Mol. Spectroscopy **5,** 355 and 390 (1960).
M. A. Thomas and H. L. Welsh, Can. J. Phys. **38,** 1291 (1960).
J. Moret-Bailly, Cahiers de Phys. **130–131,** 1 (1961).
R. A. Olafson, M. A. Thomas, and H. L. Welsh, Can. J. Phys. **39,** 419 (1961).
H. C. Allen, Jr., and E. K. Plyler, J. Research NBS **63,** 145 (1959).
E. H. Richardson, S. Brodersen, L. Krause, and H. L. Welsh, J. Mol. Spectroscopy **8,** 406 (1962).

[2] H. C. Allen, Jr., Phil. Trans. Roy. Soc. London **A253,** 335 (1961).

[3] N. Gailar and E. K. Plyler, J. Research NBS **45,** 102 (1955).

[4] E. K. Plyler, L. R. Blaine, and E. D. Tidwell, ibid., **55,** 279 (1955).

[5] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, (1955).

[6] J. K. Bragg and S. Golden, Phys. Rev. **75,** 735 (1949).

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

[8] J. K. Wilmshurst and H. J. Bernstein, Can. J. Chem. **35,** 226 (1957).

[9] G. E. MacWood and H. C. Urey, J. Chem. Phys. **4,** 402 (1936).

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