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The $A^2\Delta$–$X^2\Pi$ band system of the CD radical

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ABSTRACT

The $A^2\Delta$–$X^2\Pi$, $\Delta v = 0$ sequence of the CD radical was observed in the 22 800–24 000 cm^{-1} spectral region using a conventional spectroscopic technique. The CD molecules were formed and excited in a stainless steel hollow-cathode lamp with two anodes and filled with a mixture of He buffer gas and CD_4. The emission from the discharge was observed with a plane-grating spectrograph and recorded using a photomultiplier tube. The observed lines were assigned to the 0–0, 1–1, 2–2, and 3–3 bands. In total, 1189 transition wavenumbers were precisely measured, with an estimated accuracy of 0.003 cm^{-1}, and rotationally analyzed. In the final global fit, the present data were combined with available high-resolution measurements of the vibration–rotation transitions [Morino et al., J. Mol. Spectrosc. 174 (1995) 123–131] and pure rotational transitions [Brown and Evenson, J. Mol. Spectrosc. 136 (1989) 68–85; Halfen et al., Astrophys. J. 687 (2008) 731–736]. This procedure enabled the extraction of molecular constants for the $A^2\Delta$ and $X^2\Pi$ states of CD. The equilibrium parameters were compared with the calculations performed using the Born–Oppenheimer approximation, and a slight difference was observed in some cases due to the partial breakdown of the B–O approximation. The electronic isotopic shift, $\Delta\nu_e$, for the A–X transition was determined to be 32.105 cm^{-1}, and the shift independent of the nuclear mass coefficient, $\Delta U = 64.762(38)$ cm^{-1}, was also calculated.

1. Introduction

Due to its chemical and astrophysical significance, the CH molecule is one of the most studied free radicals. Its presence has been revealed in a number of different objects: the sun, stellar atmospheres, comets, interstellar space, flames and explosions. From a spectroscopic point of view, its energy levels are now very well characterized, based on electronic, infrared, far-infrared, and microwave spectroscopy (for a review, see [1,2] and references therein). The emission spectrum of CH in the visible and near-ultraviolet regions consists of three band systems, arising from the transitions between the excited $A^2\Delta$, $B^2\Sigma^-$, and $C^2\Sigma^+$ electronic states and the common ground $X^2\Pi$ state. In the laboratory, these systems have been extensively studied for many years, beginning with Heurlinger [3] in 1918. A summary of the analyzed systems of CH and tabulations of molecular parameters, based on data available prior to 1976, were reviewed by Huber and Herzberg [4].

In contrast, only a few studies on the electronic spectrum of the deuterated isotopologue CD have been conducted, starting with that of Shindei [5] in 1936.

The 0–0 and 1–1 bands of the $A^2\Delta$–$X^2\Pi$ system (and the fundamental bands of the B–X and C–X systems) were rotationally analyzed by Gerö [6], and some of the principal constants for all the analyzed states were derived.

The 2–2 band of the A–X system was first identified by Gerö and Schmid [7] from the position of the characteristic isolated group of lines at 4319.7 Å in the CD spectrum (corresponding to the position of the 2–2 band of CH at 4324 Å). However, in view of our current measurements, their interpretation of the spectrum was incorrect. The strong feature at 23 143 cm^{-1} (see Fig. 2) belongs to the 3–3 band, and it arises from extreme overlapping of the main Q_{11ef}, Q_{11fe}, Q_{22ef} and Q_{22fe} branches.

Herzberg and Johns measured various electronic transitions of CD (including the $D^2\Pi_i$–$B^2\Sigma^-$ and $F^2\Sigma^+$–$X^2\Pi$ transitions not observed in emission) in the ultraviolet and vacuum ultraviolet regions of absorption spectra using flash photolysis of diazomethane [8]. However, these studies derived information about the localization of several electronic states of CD and provided only rough structural information. The experimental data were of low precision, which limited the interpretation of the results.

Information on the $X^2\Pi$ state has been significantly improved through the results obtained by analyzing the vibration–rotation and pure rotational transitions in the ground state of CD. High-precision data for $v = 0$ were derived by Brown and Evenson [9] from far-infrared laser magnetic resonance (FIR LMR) spectra of the CD radical. The rotational, fine-structure, Λ-doubling, and deuterium hyperfine constants were determined from these data. Morino et al. [10] observed the 1–0 and 2–1 vibration–rotation bands using a high-resolution Fourier transform spectrometer and obtained improved constants for the ground state. Later, Wienkoop et al. [11] measured the mid- and far-infrared LMR spectra of CD

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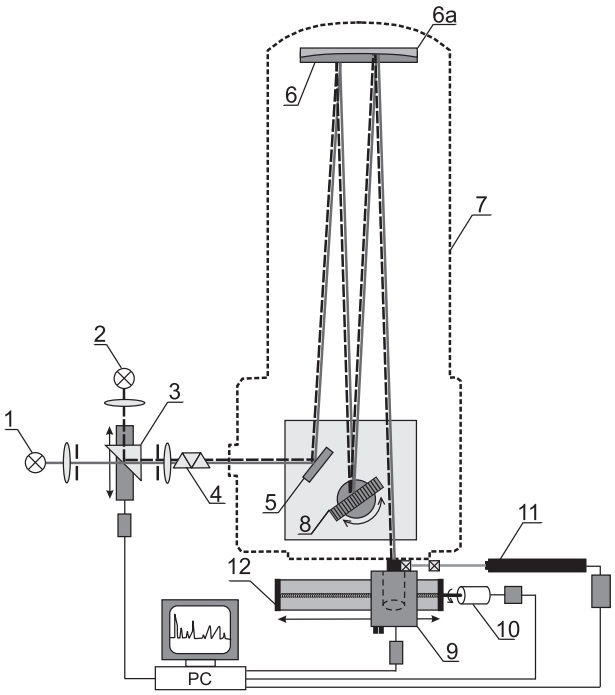
for the 1–0, 2–1, and 3–2 vibrational bands and in the excited vibrational levels $v = 1,2$. These new observations were combined with those from earlier studies of CD in the $X^2\Pi$ state [9,10] to yield an improved set of vibration–rotation parameters for this molecule. More recently, Halfen et al. [12] reported measurements for the lowest energy rotational transitions of CD ($N = 1 \leftarrow 1$ and $2 \leftarrow 1$) and ^{13}CH ($N = 1 \leftarrow 1$).

The electronic structure of the CH radical has been the subject of numerous theoretical studies (for a detailed bibliography and references, see [13]). The most accurate description of the ground and excited states of CH (along with the CD, ^{13}CH and ^{13}CD isotopic species) was reported by Kalemos et al. [13]. This work provided accurate spectroscopic constants, potential energy curves (PECs) and values of other parameters, including equilibrium distances, binding energies, vibrational and rotational interaction constants as well as dipole moments.

This work concerns the spectrum of the $A^2\Delta$–$X^2\Pi$ system of the CD molecule and is a continuation of the previous research on the various isotopic species of the CH and CH^+ molecules undertaken in our laboratory. In the framework of the present experiment, we recorded high-resolution emission spectra of CD in the 22800–24000 cm^{-1} region using a conventional spectroscopic technique. We measured and analyzed the rotational structure of four bands of the A–X system: 0–0, 1–1 (reinvestigations) and 2–2 and 3–3 (first analyses). Our measurements of CD rotational lines are in agreement with the previous values of Gerö [6] where they overlap; however, the precision of the line wavenumbers has been improved by approximately an order of magnitude. Moreover, the full rotational structure of the bands (12 clearly resolved branches) was observed for the first time. The present data, when combined with previous vibrational–rotational transition data [10] and pure rotational transition data [9,12], provide improved spectroscopic constants for the ground $X^2\Pi$ state and particularly the first excited state $A^2\Delta$ of the CD radical.



1 - hollow-cathode tube, 2 - reference spectrum (Th lamp),
3 - moving fused silica prism, 4 - Amici prism,
5 - reflecting mirror, 6 - flat reflecting mirror,
6a - parabolic mirror, 7 - optical tube,
8 - plane grating, 9 - photomultiplier tube + cooler,
10 - stepper motor + planetary transmission,
11 - laser interferometer, 12 - linear stage.

Fig. 1. Experimental setup.

2. Experimental details

The CD molecules were produced and excited by an electric discharge in a water-cooled, stainless steel hollow-cathode lamp with two anodes [14]. The anodes were operated at 2×430 V and 2×50 mA dc. A non-flowing mixture of 6.0 Torr He buffer gas and 2.0 Torr CD_4 (98% of D) was observed to be optimal in producing $A^2\Delta$–$X^2\Pi$ emission.

The spectra were observed in the 6th order using a 2-m Ebert plane-grating PGS-2 spectrograph equipped with 651-grooves/mm grating with a total of 45600 grooves, blazed at 1.0 μm. The reciprocal dispersion was in the range of 0.067–0.071 nm/mm, and the theoretical resolving power was approximately 270000. The CD spectra were recorded by translating an exit slit and photomultiplier tube (HAMAMATSU R943-02) on a linear stage (HIWIN KK5002) along the focal curve of the spectrograph. The entrance and exit slit widths were 0.035 mm. The line intensities were measured using single photon counting (a HAMAMATSU C3866 photon counting unit and M8784 photon counting board) with a counter gate time of 200 ms (no dead time between the gates). The positions of the exit slit were measured using a He–Ne laser interferometer (LASERTEX) synchronized with the photon counting board. During the counter gate time, the position was measured 64 times, and a mean value of the position with the counts number were transmitted to a PC as a measurement point. The total number of the measurement points was approximately 73000 for one scan using a sample step of 3 μm (the sample step is the translation of the exit slit during the counter gate time). For apparatus details, see Fig. 1.

This type of spectrograph is very sensitive to mechanical and thermal deformation of its solid, optical tube. Variations in the atmospheric pressure and optical alignment of the spectroscopic lamps have comparable effects on line positions (a few microns). To reduce fluctuations in the line positions, the apparatus was thermally insulated and mounted on the main wall with channel iron and a 6-cm thick granite plate, and the temperature in the laboratory was stabilized using an air conditioner with 0.2 °C accuracy. Moreover, the optical alignment of the CD and reference lamps was corrected to obtain the same light distribution along the exit slit. Replication of the line position measurements was measured to be 0.2–0.5 μm, according to the variations in atmospheric pressure.

Simultaneously recorded thorium atomic lines [15] obtained from several overlapped orders of the spectrum from a water-cooled hollow-cathode tube were used for absolute wavenumber calibration. The peak positions of the spectral lines were calculated using a least-squares procedure and assuming a Gaussian line-shape for each spectral contour (30 points per line, with an uncertainty of the peak position for a single line of approximately 0.1–0.2 μm). For the wavenumber calculations, seventh-order interpolation polynomials were used. The typical standard deviation of the least-squares fit for the 70–80 calibration lines was approximately 0.0015 cm^{-1}. The accuracy of the calibration procedure was measured to be ± 0.0015 cm^{-1} (using two Th lamps simultaneously - one as an examination light source and the other to provide the reference spectrum). The CD lines have spectral widths of approximately 0.15—0.18 cm^{-1} and appear with a maximum signal-to-noise ratio of approximately 80:1 for the strongest 0–0 band (the most intense lines produced a count rate of approximately 32000 photons/s). The final calculations of the positions of the molecular line centers were supported by an earlier set of sorted wavenumbers for the CD and CH lines in the measured region obtained from preliminary measurements.

Table 1
Summary of observations and analyses of the $A^2\Delta$–$X^2\Pi$ band system, vibration–rotation bands, and pure rotational transitions of CD.

Band	Remarks	Band origin[a]	Total number of lines	J_{max}	f[b]	σ[c]$\times 10^3$ (in cm^{-1})
A–X transition						
0–0	Reinvest.	23201.12020(45)	446	38.5	370	3.18
1–1	Reinvest.	23216.57792(61)	348	32.5	270	3.60
2–2	First anal.	23199.6378(12)	240	26.5	161	6.57
3–3	First anal.	23142.9287(22)	155	20.5	98	8.80
Vibrational–rotational transition[d]						
1–0	Reanal.	2032.03404(27)	53	9.5	27	1.13
2–1	Reanal.	1963.72099(35)	48	8.5	26	1.20
Pure rotational transition						
	Reanal.		28[e]	5.5	16	0.016

[a] In cm^{-1}, 1σ in parentheses.
[b] Number of degrees of freedom of the fit for the individual band analysis.
[c] Standard deviation of the fit for the individual band analysis.
[e] Brown and Evenson [9]. Three wavenumber values were substituted with the values calculated by B.J. Drouin from Halfen et al. [12] measurements (see text).
[d] *Morino et al. [10].*

Consequently, the measurements of the strong and unblended lines are expected to be accurate to ± 0.003 cm^{-1}. However, some weaker and blended lines were measured with a decreased accuracy of ± 0.006 cm^{-1}. In total, 1189 lines belonging to the 0–0, 1–1, 2–2 and 3–3 bands of CD were measured, and their wavenumbers are provided in the Supplementary material section.

3. Description of the spectra

The present spectra contain the 0–0, 1–1, 2–2 and 3–3 vibrational bands belonging to the $A^2\Delta$–$X^2\Pi$ transition observed in the 22800–24000 cm^{-1} region. These $\Delta v = 0$ bands lie in the same spectral region (see band origin values in Table 1), which causes their extreme overlapping and makes spectra interpretation very complicated. The 0–0 band is the strongest, and the 1–1, 2–2, and 3–3 bands represent approximately 60%, 30%, and 10% of the intensity of the 0–0 band, respectively. The off-diagonal bands ($\Delta v = \pm 1$) were very weak and could not be observed. The rotational structure of the $^2\Delta$–$^2\Pi$ bands depends on the coupling case to which both states taking part in the transition belong [16]. As long as both states belong to the same coupling case (Hund's case (a) or Hund's case (b)), six intense main branches are present: P_1, P_2, Q_1, Q_2, R_1, and R_2, each of which is doubled by Λ-doubling in the $^2\Pi$ state. In the most general case, if the two terms belong to different coupling cases, 24 branches are present. For CD, the $A^2\Delta$ state changes from approximately Hund's case (a) to Hund's case (b) as J increases and several satellite branches are allowed. In total, six additional satellite branches ($R_{12}, Q_{12}, P_{12}, R_{21}, Q_{21}$, and P_{21}) are expected in each sub-band. The complete rotational structure described above was not measured in all the recorded bands because of the extreme overlapping of the bands.

A part of the spectrum of the $A^2\Delta$–$X^2\Pi$ transition of CD in the region of 23100 cm^{-1} is presented in Fig. 2. Several low-J, -P_{11ee}, -P_{11ff}, -P_{22ee}, and -P_{22ff} lines of the 0–0, 1–1, and 2–2 bands have been marked.

4. Analysis and results

The reduction of the line wavenumbers (see Supplementary material) to rovibronic parameters was performed using an individual band-by-band analysis and an unweighted nonlinear least-squares fitting procedure using the computer program described earlier [17]. In this program, both analyzed states are represented by effective Hamiltonians from Brown et al. [18].

Direct matrix elements for the $^2\Pi$ state were used in the form proposed by Amiot et al. [19] with a slight modification; i.e., the signs of the matrix elements for the constant L were changed to be opposite to those used in the original work [19] to preserve the commonly used convention. For that reason, the signs of the L constants in our previous works [24,25] differ from those obtained here. The matrix elements of the $^2\Delta$ state were taken in the original form given by Brazier and Brown [20]. The explicit matrix elements used in our calculations are available from our website [21] or from Table IV of the Supplementary material.

To combine our results with those obtained earlier, we have performed a fit of the available data on the CD radical in its $X^2\Pi$ state (see Table 1). The refitted data set is composed of the following:

(i) the FTIR measurements (1–0 and 2–1 bands) of Morino et al. [10],
(ii) the hyperfine-free line positions calculated by Brown and Evenson [9] from their far-infrared LMR data ($v = 0$),
(iii) the hyperfine-free line positions calculated[1] for us by B.J. Drouin from fundamental rotational transitions data ($v = 0$) of Halfen et al. [12].

Because the last two data sets overlapped, they were integrated and fitted together as a single data set. If two wavenumber values were available for the same line, the slightly more accurate value was selected. Three line wavenumbers ($R_{12ff}(0.5)$, $R_{12ee}(0.5)$ and $Q_{21ef}(1.5)$) in the Brown and Evenson [9] data were substituted with the values calculated by B.J. Drouin from Halfen et al. [12] measurements.

The procedure which combines these two data sets was required for two reasons. First, the limited number of rotational transitions observed by Halfen et al. [12] precluded the determination of the full set of the molecular constants of the $X^2\Pi$, $v = 0$ vibronic level, which is desirable in conducting a global merge calculus trial. Second, these two measurements were not consistent and thus resulted in slightly different values for the main molecular parameters of the $v = 0$ level of the ground state of CD. For example, $B_0 = 7.7018682(16)$ constant of [9] compares with the value of 7.701829(9) [12] (for a detailed comparison, see Table V [9] and Table 3 [12]).

In this way a set of 28 pure rotational transitions has been obtained (see Table 1 and Table III in Supplementary material), which has become the subject of our further analysis. The initial fit

[1] $R_{12ff}(0.5) = 439262.229(100)$ MHz, $R_{12ee}(0.5) = 439798.901(100)$ MHz, $Q_{21ef}(1.5) = 884775.254(200)$ MHz, $R_{11ff}(1.5) = 915853.1(10)$ MHz, $R_{11ee}(1.5) = 916954.5(10)$ MHz.

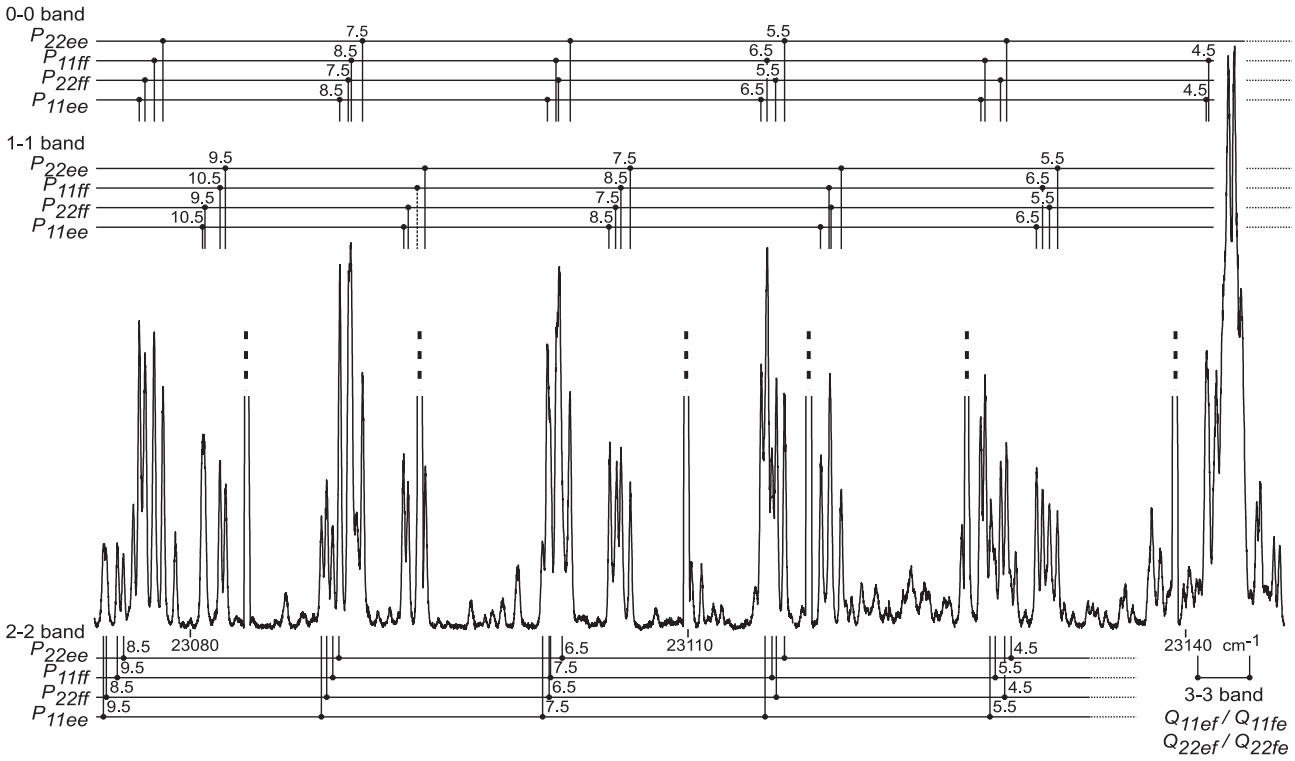


Fig. 2. Part of the rotational structure of the 0–0, 1–1, and 2–2 bands of the $A^2\Delta$–$X^2\Pi$ transition of CD. Only the strongest branches have been rotationally interpreted (the other lines are represented by the unmarked lines). The strong feature at 23 142 cm^{-1} arose from the extreme overlapping of the four main Q branches of the 3–3 band. The Th atomic lines used for calibration are marked with broken lines.

showed that the inclusion of all line positions in the calculation did not give satisfactory results because:

- lines $R_{12ff}(0.5)$ and $R_{12ee}(0.5)$ deviated from the model by the value of about 400 kHz while their accuracy assessed by B.J. Drouin amounted to 100 kHz,
- the obtained molecular parameters were not in agreement with those achieved from the individual fit of the 0–0 band of the A–X system. The evidence of this was the unsatisfactory value of the estimated variance of the merging of both sets of constants.

The next step was to recognize the lines responsible for discrepancies between the sets of the ground state molecular parameters, described above. We used the precise constants for the $X^2\Pi$, $v = 0$ level obtained on the basis of our measurements (12 branches with $J_{max} = 38.5$, $\sigma = 0.0032$ cm^{-1}, $f = 370$) of the 0–0 band of the $A^2\Delta$–$X^2\Pi$ transition in the reduction of the pure rotational transitions. In this fit most of the molecular constants were constrained, except the major ones: B, A, γ, p, and q. We found that among all the lines used seven showed substantial deviation from the model. Our observations have coincided with the information concerned the weights and intensities of rotational transitions (see Tables IV and VII [9]) given in the work of Brown and Evenson [9]. For the reasons described above, it has been decided to exclude these seven rotational transitions from further calculations (see Table III in Supplementary material).

Because Wienkoop et al. [11] did not provide the hyperfine free frequencies for their far-infrared LMR spectra ($v = 1$ and 2 vibrational level) and from the mid-infrared CO LMR spectra (1–0, 2–1 and 3–2 band), we could not include these data in our refitting procedure. The statistical data of the individual band fits are presented in Table 1.

The molecular constants obtained from the individual fits were subsequently used as input data for the merge calculations described by Albritton et al. [22] and Coxon [23]. In this method, the output molecular constants and the accompanying variance–covariance matrices from each of the individual fits of the bands are taken together as input for a correlated least-squares fit, which then yields the desired merged single values. This merging is equivalent to a global fit of all the data to the parameter sets for both states; however, it is more precise, revealing prospective strong correlations between molecular parameters or systematic errors of wavenumber measurements. The estimated variance of this merging was $\sigma_M^2 = 1.25$, and the number of degrees of freedom was $f_M = 48$. The value of variance is satisfactory and lies within the 95% confidence limits of a χ^2/f_M distribution, which excludes the existence of systematic errors in the line wavenumbers of the analyzed bands.

In this manner, the final molecular parameters for the $X^2\Pi$, $v = 0, 1, 2$ and $A^2\Delta$, $v = 0, 1, 2$ states were derived. As the merge program requires the bands to have at least one common vibrational level, the 3–3 band was excluded from the merge calculation. All of the values of the molecular parameters for the $v'' = 3$ and $v' = 3$ levels originate from the individual 3–3 band fit.

The resulting molecular constants are compared with the calculations performed within the Born–Oppenheimer approximation for the $X^2\Pi$ state in Table 2 and for the $A^2\Delta$ state in Table 3.

The main $X^2\Pi$ state molecular constants of $v = 0$ are known with excellent precision from previous studies [9,11,12] of the CD ground state. However, we observed that using these molecular parameters, obtained from a limited number of rotational transitions, the reduction of the A–X 0–0 band proved unsatisfactory. With constrained X-state constants, the least squares fit had a large standard deviation of $\sigma = 0.072$ cm^{-1}.

Table 2
Molecular constants (in cm^{-1}, 1σ in parentheses) of the $X^2\Pi$ state of CD.

Constant	$v=0$	$v=1$	$v=2$	$v=3$
T_v	0.0	2032.03419(27)	3995.75544(45)	5891.7963[c]
B_v	7.70187357(50) 7.689281[a]	7.4910076(75) 7.478695[a]	7.281586(16) 7.269631[a]	7.07342(12) 7.061812[a]
$D_v \times 10^4$	4.27932(17) 4.2582[a]	4.22821(33) 4.2073[a]	4.1746(11) 4.1596[a]	4.1134(42) 4.1149[a]
$H_v \times 10^8$	1.8087(24) 1.8266[a]	1.7895(27) 1.7927[a]	1.684(12) 1.7528[a]	1.656(54) 1.7067[a]
$L_v \times 10^{12}$	−0.9984(97) −1.228[a]	−1.204[a,b]	−1.198[a,b]	−1.210[a,b]
A_v	28.096366(37) 28.1207[a]	28.2361(16) 28.2632[a]	28.3722(24) 28.4025[a]	28.512[b,c] 28.5385[a]
$\gamma_v \times 10^2$	−1.41445(55) −1.3832[a]	−1.3583(71) −1.3223[a]	−1.328(12) −1.2614[a]	−1.269(16) −1.2004[a]
$\gamma_{Dv} \times 10^6$	2.36(15) 2.520[a]	2.435[a,b]	2.394[a,b]	2.395[a,b]
$p_v \times 10^2$	1.81775(40) 1.8078[a]	1.7184(49) 1.7494[a]	1.635(11) 1.6909[a]	1.618(29) 1.6325[a]
$p_{Dv} \times 10^6$	−2.530(37) −2.661[a]	−2.446[a,b]	−2.231[a,b]	−2.016[a,b]
$q_v \times 10^2$	1.131706(51) 1.12908[a]	1.09953(32) 1.09953[a]	1.06976(87) 1.06999[a]	1.0408(31) 1.04044[a]
$q_{Dv} \times 10^6$	−2.3715(30) −2.380[a]	−2.2869(48) −2.335[a]	−2.271(19) −2.290[a]	−2.210(97) −2.245[a]
$q_{Hv} \times 10^{10}$	2.232(24) 2.403[a]	2.344[a,b]	2.285[a,b]	2.226[a,b]

[a] The value calculated from the ^{12}CH parameters of Ref. [24] using the isotopic relationship within the Born–Oppenheimer approximation.
[b] Fixed value.
[c] Obtained from the equilibrium parameters reported by Wienkoop et al. [11].

Table 3
Molecular constants (in cm^{-1}, 1σ in parentheses) of the $A^2\Delta$ state of CD.

Constant	$v=0$	$v=1$	$v=2$	$v=3$
T_v	23201.12020(45)	25248.61211(67)	27195.3933(13)	29034.7249[c]
SSS B_v	7.9014090(59) 7.905785[a]	7.641573(14) 7.645763 [a]	7.368010(24) 7.372263[a]	7.076599(99) 7.080109[a]
$D_v \times 10^4$	4.53038(26) 4.5338[a]	4.59470(66) 4.6174[a]	4.6990(13) 4.7084[a]	4.8844(21) 4.8704[a]
$H_v \times 10^8$	1.4975(33) 1.5873[a]	1.2191(98) 1.2668[a]	0.710(13) 0.9463[a]	0.626[a,b]
$L_v \times 10^{12}$	−1.868(13) −2.252[a]	−2.235(49) −2.249[a]	−2.245[a,b]	−2.240[a,b]
A_v	−1.09071(77) −1.10456[a]	−1.0670(11) −1.08290[a]	−1.0651(19) −1.05935[a]	−1.0328(29) −1.03390[a]
$\gamma_v \times 10^2$	2.2730(43) 2.2942[a]	2.177(10) 2.2028[a]	2.090(15) 2.1113[a]	2.020[a,b]
$\gamma_{Dv} \times 10^6$	−2.78(16) −2.709[a]	−2.63(11) −2.594[a]	−2.479[a,b]	−2.363[a,b]
$p_v \times 10^7$	1.52(36) 3.04[a]	2.13(91) 5.84[a]	8.63[a,b]	11.40[a,b]
$q_v \times 10^8$	−0.458(57) −0.258[a]	−1.84(19) −3.47[a]	−6.67[a,b]	−9.88[a,b]

[a] The value calculated from the ^{12}CH parameters of Ref. [24] using the isotopic relationship within the Born–Oppenheimer approximation.
[b] Fixed value.
[c] Obtained from the 3–3 band origin value (Table 1) and T_3 value (Table 2).

In addition, some comments should be made about the present H_0 constant of the X state. In previous studies [9,11,12], this constant had to be fixed in the fits, mostly due to the small number of rotational transitions recorded. The constrained H_0 constant value of 1.585×10^{-8} cm^{-1} was calculated from CH parameters. In this study, we have recorded a very wide spectrum for the 0–0

band of the $A^2\Delta$–$X^2\Pi$ system (12 branches with $J_{max} = 38.5$), and the H_0 and L_0 constants could be determined with satisfactory precision. The present value of H_0 is $1.8087(24) \times 10^{-8}$ cm^{-1}. Assuming a traditional isotopic relationship for H_e and using our previous CH data [24], we obtain a value of 1.8266×10^{-8} cm^{-1} for H_0 of CD, which is in reasonable agreement with the present experimental value. Table 2 demonstrates that we have determined the five principal Λ-doubling parameters for the $v = 0$ vibronic level of the ground state. Four of them (p_0, p_{D_0}, q_0, and q_{D_0}) have been previously reported [11,12]. In general, our results confirm the previous ones, except for the p_{D_0} value, which is larger in magnitude (by a factor of about 1.6) than that reported by Wienkoop et al. [11] and Halfen et al. [12].

The B_v, D_v, A_v, γ_v, p_v, q_v and q_{Dv} molecular constants for the $v = 1$ and 2 levels of the X state of CD have only been previously reported by Morino et al. [10] from their FTIR measurements. Our results (Table 2) are in agreement with those obtained earlier [10], mostly within the quoted errors. However, many of the earlier results have been improved by an order of magnitude. For example, our lambda-doubling constants $p_1 = 1.7184(49) \times 10^{-2}$ cm^{-1} and $q_1 = 1.09953(32) \times 10^{-2}$ cm^{-1} can be compared with the values of $1.725(12) \times 10^{-2}$ cm^{-1} and $1.1094(30) \times 10^{-2}$ cm^{-1}, respectively.

Only one set of published experimental results is available for the $X^2\Pi$, $v = 3$ vibronic level, that of Herzberg and Johns [8], from the analysis of the absorption spectrum of the C–X system of CD. Only estimated values for the main molecular constants were presented: $B_3 = 7.077(4)$ cm^{-1}, $D_3 = 4.5(4) \times 10^{-4}$ cm^{-1} and $q_3 = 0.006(2)$ cm^{-1}. The present main molecular constants can be compared with the values reproduced from the $X^2\Pi$ state equilibrium parameters of Wienkoop et al. [11]. For example, our experimental $B_3 = 7.07342(12)$ cm^{-1} constant compares with the calculated value of 7.07386 cm^{-1}.

In Table 2, we compare the results of the present study with those values calculated from the CH parameters [24] within the Born–Oppenheimer approximation. As observed, some constants have been constrained in the fit to the values estimated from these calculations.

Finally, the present $X^2\Pi$ state molecular constants (especially for the $v = 0$ vibronic level) are observed to be more reliable than those published earlier [9–12], mainly because we have been able to combine the available $X^2\Pi$ state data [9,10,12] with the present wide measurements of the bands of the $A^2\Delta$–$X^2\Pi$ transition of CD. The constants from Table 2 for the $X^2\Pi$ state supersede those previously reported from the ground state transitions measurements and minor discrepancies existing thus far. It should be stressed that the new constants reproduce the fundamental transitions $R_{12ee}(0.5)$ and $R_{12ff}(0.5)$ calculated by B.J. Drouin from Halfen et al. [12] measurements with an accuracy greater than 100 kHz (see Table III in Supplementary material).

The principal molecular constants of the $A^2\Delta$, $v = 0$, 1 vibronic levels of CD were first published by Gerö [6] and were recently reproduced by Herzberg and Johns [8]. These very approximate previous results were determined to be in agreement with our results for B_0, D_0, B_1, and D_1. For example, our $B_0 = 7.9014090(59)$ cm^{-1}

Table 4
Equilibrium molecular constants (in cm^{-1}, 1σ in parentheses) for the $X^2\Pi$ and $A^2\Delta$ states of CD.

Constant	$X^2\Pi$			$A^2\Delta$	
	This work	Ref. [11]	Calculated by scaling[a]	This work	Calculated by scaling[a]
ν_e	–	–		23183.5751(24)	23151.4925
ω_e	2101.05304(93)	2101.05193(55)	2100.4490	2141.7459(64)	2139.6188
$\omega_e x_e$	34.72811(36)	34.72785(58)	34.73849	45.3023(43)	43.8823
$\omega_e y_e$	0.14147[b]	0.14147(10)	0.14396	−1.12292(77)	−1.34107
$\omega_e z_e \times 10^2$	−0.4481[b]	−0.4481[b]	−0.4469		
B_e	7.8079371(70)	7.8079823(55)	7.795231	8.027467(56)	8.032360
α_e	0.212582(18)	0.212240(11)	0.212373	0.25006(16)	0.25150
$\gamma_e \times 10^3$	0.9322(68)	0.7120(32)	0.9682	−3.77(11)	−2.857
$\varepsilon_e \times 10^4$	−0.46[a,b]		−0.46	−6.87(22)	−8.63
$D_e \times 10^4$	4.30522(65)	4.27683(41)	4.28482	4.5004(24)	4.4750
$\beta_e \times 10^6$	−5.165(73)	−3.83(13)	−5.398	6.37(68)	13.69
$\delta_e \times 10^6$				−1.09(45)	−4.39
$\zeta_e \times 10^7$				6.85(81)	10.58
$H_e \times 10^8$	1.824(16)		1.8412	1.6367(70)	1.7475
$\alpha_{He} \times 10^9$	−0.23(14)		−0.278	−2.78(11)	−3.205
$\beta_{He} \times 10^{11}$	−3.04[a,b]		−3.04		
$L_e \times 10^{12}$			−1.246	−1.685(32)	−2.254
$\alpha_{Le} \times 10^{14}$			4.17	−36.7(51)	0.372
$\beta_{Le} \times 10^{16}$			−0.90		
A_e	28.025518(87)	28.02402(44)	28.04818	−1.1004(29)	−1.1147
α_{Ae}	0.14243(18)	0.14548(87)	0.14582	0.0208(25)	0.0198
$\beta_{Ae} \times 10^3$	−1.46[b]	−1.46(29)	−1.642		0.948
$\gamma_e \times 10^2$	−1.4387(19)	−1.44415(45)	−1.41365	2.3192(23)	2.3399
$\alpha_{\gamma_e} \times 10^4$	4.85(35)	6.104(74)	6.092	−9.29(24)	−9.14
$\gamma_{D_e} \times 10^6$					−2.767
$\alpha_{\gamma_{D_e}} \times 10^7$					1.152
p_e	$1.8656(21) \times 10^{-2}$		1.8370×10^{-2}	$1.22(71) \times 10^{-7}$	1.648×10^{-7}
α_{p_e}	$-9.58(40) \times 10^{-4}$		-5.84×10^{-4}	$0.61(98) \times 10^{-7}$	2.79×10^{-7}
q_e	$1.14753(27) \times 10^{-2}$		1.14385×10^{-2}	$0.23(13) \times 10^{-8}$	1.35×10^{-8}
α_{q_e}	$-3.166(47) \times 10^{-4}$		-2.955×10^{-4}	$-1.38(20) \times 10^{-8}$	-3.21×10^{-8}
$q_{D_e} \times 10^6$	−2.4132(48)		−2.4022		
$\alpha_{q_{D_e}} \times 10^8$	8.38(53)		4.50		

[a] The value calculated from the ^{12}CH parameters of Ref. [24] using the isotopic relationship within the Born–Oppenheimer approximation.
[b] Fixed value.

and $B_1 = 7.641573(14)\ cm^{-1}$ constants compare well with the previous values of $7.902\ cm^{-1}$ and $7.642\ cm^{-1}$, respectively. As observed in Table 3, a wide set of molecular constants for the A state were experimentally obtained for the first time. Some of the smaller parameters (especially for the $v = 2$ and 3 vibronic levels) had to be constrained to the values estimated from isotopic calculations within the Born–Oppenheimer approximation.

4.1. Equilibrium parameters of the $X^2\Pi$ and $A^2\Delta$ states

Based on the values obtained for the rovibronic constants and assuming their traditionally recognized polynomial dependence on the vibrational quantum number, the equilibrium molecular parameters for the $X^2\Pi$ and $A^2\Delta$ states were calculated using a weighted least-squares method. The results are presented in Table 4 and are compared with the values calculated from the CH parameters [24] and with recent experimental values reported by Wienkoop et al. [11] for the X state of CD.

The ω_e and $\omega_e x_e$ vibrational constants for the ground state were calculated based on the vibrational term values (see Table 2) and with the $\omega_e y_e$ and $\omega_e z_e$ parameters fixed to the values derived in work [11]. The excellent compatibility of our results and those reported by Wienkoop et al. [11] (particularly for the vibrational and rotational parameters) is not surprising because the same experimental material for the X state was partially used in both studies.

The main rotational parameters of the A state are in agreement with these scaled from the constants of CH [24], except a few minor ones, i.e. α_{Le} and q_e. The observed discrepancies result from the fact that the equilibrium parameters of the $A^2\Delta$ state of CH used for isotopic calculations were based on molecular parameters obtained from a limited number of rotational transitions.

The 0–0 to 3–3 band origin values (see Table 1) were used to evaluate the equilibrium vibrational constants for the $A^2\Delta$ state. Small differences between the present experimental results and those obtained by isotopic scaling arise primarily from a breakdown of the Born–Oppenheimer approximation. This problem have been previously discussed by Morino et al. [10] and by Wienkoop et al. [11]. The present experimental vibrational constants $\omega_e^X = 2101.05304(93)$, $\omega_e x_e^X = 34.72811(36)$, $\omega_e^A = 2141.7459(64)$, and $\omega_e x_e^A = 45.3023(43)$ can be compared with the theoretical values derived by Kalemos et al. [13]. The values obtained in work [13] were $2093.3\ cm^{-1}, 33.64\ cm^{-1}$ for the X state and $2137.4\ cm^{-1}, 49.39\ cm^{-1}$ for the A state. The B_e constants were used to determine the equilibrium bond lengths $r_e = 1.11886609(50)$ Å and $r_e = 1.1034610(38)$ Å for the $X^2\Pi$ and $A^2\Delta$ states, respectively.

The present value of $v_e = 23183.5751(24)\ cm^{-1}$ for the A–X transition of CD can be compared with the value of 23151.4925 (13) of CH [24] and with the value 23151.8930(57) of ^{13}CH [25]. The differences observed between these values made it possible to derive the electronic isotope shift for the A–X transition, as described in detail by Bunker [26], using the expression:

$$\Delta v_e = v_e^i - Y_{00}'^i + Y_{00}''^i - (v_e - Y_{00}'^{CH} + Y_{00}''^{CH}). \quad (1)$$

The electronic isotopic shifts derived in this manner are presented in Table 5, along with all of the data used in the calculations.

The accuracy of the derivation of the Δv_e values is impossible to determine for the reason discussed in detail in [26]. In the same work, Bunker demonstrated that Δv_e can be written in the form

$$\Delta v_e = \Delta U(1 - \rho^2)/\mu \quad (2)$$

where ΔU is independent of the nuclear masses, and $\rho = (\mu/\mu^i)^{\frac{1}{2}}$. Using a linear least-squares fitting procedure and data from Table 5, we obtained a value of $\Delta U = 64.762(38)\ cm^{-1}$. Eq. (2) can be applied for future analysis of other isotopic species of this molecule for a more precise determination of ΔU and for estimation of the precision of the electronic isotopic shifts of all species of this molecule.

Table 5
Electronic isotopic shift of the $A^2\Delta$–$X^2\Pi$ system of the three isotopologues of CH.[a]

Molecule	Ref.	v_e	Y'_{00}	Y''_{00}	Δv_e
CH	[24]	23151.4925(13)	0.9289	1.7625	
^{13}CH	[25]	23151.8930(57)	0.9216	1.7526	0.3979
CD	This work	23183.5751(24)	0.0915	0.9474	32.1049

[a] In $cm^{-1}, 1\sigma$ in parentheses.

5. Conclusions

The full rotational structure of the 0–0, 1–1, 2–2 and 3–3 bands of the $A^2\Delta$–$X^2\Pi$ system of CD has been observed for the first time. Although this transition has been observed previously [5–7], our work shows improvements in the measured rotational line positions. The bands were analyzed using the effective Hamiltonian proposed by Brown et al. [18]. In the final fit, the present data were combined with available experimental results concerning the ground $X^2\Pi$ state of CD [9,10,12]. In this manner, a wide set of molecular constants for both considered states were obtained.

A comparison of the present equilibrium parameters with those calculated from CH parameters [24], using the isotopic relationship within the B–O approximation, reveals small discrepancies from this approximation. The electronic isotopic shift, $\Delta v_e = 32.105\ cm^{-1}$, and that independent of the nuclear masses coefficient, $\Delta U = 64.762(38)\ cm^{-1}$, were determined. Therefore, we consider that the present results significantly widen and improve the existing information on the spectrum and energetic structure of the CD molecule.

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2012.05.006.

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