

Isotopomer Dependence and Born-Oppenheimer Breakdown in Mid and Far Infrared Spectra of CdH

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Objectives of Spectroscopic Data Analysis

- **Data reduction:** *to provide a compact and accurate representation of all available data.*
- **Interpolation:** *to provide a means of making reliable predictions for missing data within the range of existing measurements.*
- **Extrapolation:** *to provide a means of making reliable (or at least plausible) predictions beyond the range of existing measurements.*
- **Physics:** *to determine physically interesting parameters or properties of the system.*

The present talk will:

- present new very high resolution far-IR data for the ground states of CdH and CdD
- present a unified analysis of all available high resolution IR and far-IR data for 14 isotopomers of CdH and CdD, which incorporates mass-scaled spin-rotation parameters

Previous High Resolution Mid-IR Work

“The ground state infrared spectra of several isotopic forms of the **CdH** and **ZnH** radicals”

R.-D. Urban, U. Magg, H. Birk and H. Jones, *J. Chem. Phys.* **92**, 14–21 (1990).

- Measured 270 lines of the 1–0 and 2–1 bands of 8 isotopomers of CdH, with estimated line position uncertainties of $\pm 0.001 \text{ cm}^{-1}$.
- Performed both individual and combined(Cd)-isotopomer Dunham fits to the level energy expression

$$E_{v,J} = \sum_m \sum_l Y_{l,m}^{(\alpha)} (v + \frac{1}{2})^l [N(N+1)]^m + \begin{cases} \frac{1}{2} N \sum_m \sum_l \gamma_{l,m} (v + \frac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N + \frac{1}{2} \\ \frac{1}{2}(N+1) \sum_m \sum_l \gamma_{l,m} (v + \frac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N - \frac{1}{2} \end{cases}$$

- in which $Y_{l,m}^{(\alpha)} = Y_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2}$, but **no** mass scaling was used for the $\gamma_{l,m}$ coefficients, and
- **no** Born-Oppenheimer breakdown coefficients were required.

“Diode laser spectroscopy of the four radicals **CdD**, **ZnD**, **BaD** and **SrD** in their $^2\Sigma$ ground state”

H. Birk, R.-D. Urban, P. Polomsky and H. Jones, *J. Chem. Phys.* **94**, 5435–5442 (1991).

- Measured 210 lines of the 1–0 and 2–1 bands of 6 isotopomers of CdD, with estimated line position uncertainties of $\pm 0.001 \text{ cm}^{-1}$.
- Performed a unified 14-isotopomer Dunham-type analysis of their Mid-IR data for CdH and CdD which included Born-Oppenheimer breakdown corrections ($\delta_{l,m}^{\text{Cd}}$ and $\delta_{l,m}^{\text{H}}$) for vibration and rotation

$$E_{v,J}^{(\alpha)} = \sum_m \sum_l \left\{ Y_{l,m}^{(1)} + \frac{\Delta M_{\text{Cd}}^{(\alpha)}}{M_{\text{Cd}}^{(\alpha)}} \delta_{l,m}^{\text{Cd}} + \frac{\Delta M_{\text{H}}^{(\alpha)}}{M_{\text{H}}^{(\alpha)}} \delta_{l,m}^{\text{H}} \right\} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \frac{1}{2})^l [N(N+1)]^m$$

as well as isotopomer mass scaling for the $^2\Sigma$ spin-rotation splittings

$$+ \begin{cases} \frac{1}{2} N \sum_m \sum_l \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \frac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N + \frac{1}{2} \\ -\frac{1}{2}(N+1) \sum_m \sum_l \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \frac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N - \frac{1}{2} \end{cases}$$

Previous Very High Resolution Far-IR Work

“The isotopic dependence of the spin-rotation interaction: the rotational spectrum of cadmium hydride in its $X^2\Sigma^+$ state” T.D. Varberg and J.C. Roberts, *J. Mol. Spectrosc.* **223**, 1-8 (2004).

- *Extensive measurements of pure rotational transitions in the $v = 0$ level of 6 isotopomers of each of CdH and CdD, with estimated line position uncertainties of ca. $\pm 0.000\,002\text{ cm}^{-1}$.*
- Resolved and assigned both spin-rotation splittings and hyperfine structure due to the ^{111}Cd , ^{113}Cd , ^1H and ^2H nuclei.
- *Performed a unified 12-isotopomer Dunham-type analysis of their Mid-IR data for CdH and CdD which included Born-Oppenheimer breakdown parameters ($\delta_{0,m}^{\text{Cd}}$ and $\delta_{0,m}^{\text{H}}$) for both atoms.*

$$E_{v,J}^{(\alpha)} = \sum_m \left\{ Y_{0,m}^{(1)} + \frac{\Delta M_{\text{Cd}}^{(\alpha)}}{M_{\text{Cd}}^{(\alpha)}} \delta_{0,m}^{\text{Cd}} + \frac{\Delta M_{\text{H}}^{(\alpha)}}{M_{\text{H}}^{(\alpha)}} \delta_{0,m}^{\text{H}} \right\} \left(\frac{\mu_1}{\mu_\alpha} \right)^m [N(N+1)]^m$$

as well as isotopomer mass scaling for the $^2\Sigma$ spin-rotation splittings

$$+ \begin{cases} \frac{1}{2} N \sum_m \gamma_{0,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^m [N(N+1)]^{m-1} & \text{for } J = N + \frac{1}{2} \\ -\frac{1}{2}(N+1) \sum_m \gamma_{0,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^m [N(N+1)]^{m-1} & \text{for } J = N - \frac{1}{2} \end{cases}$$

Their analysis treated all 12 isotopomers simultaneously, but considered only their pure rotational $v=0$ data.

However ... they were *not* able to obtain an adequate fit unless

- independent $\delta_{0,1}^{\text{Cd}}(\text{CdH})$ and $\delta_{0,1}^{\text{Cd}}(\text{CdD})$ B-O-breakdown parameters were introduced (in addition to fitted $\delta_{0,2}^{\text{Cd}}$ and $\delta_{0,1}^{\text{H}} - \delta_{0,4}^{\text{H}}$ values)!
- H- and Cd-atom B-O-breakdown parameters were introduced for treating the $^2\Sigma$ spin-rotation splitting: $\gamma_{0,m}^{(\alpha)} = \left\{ \gamma_{0,m}^{(1)} + \frac{\Delta M_{\text{Cd}}^{(\alpha)}}{M_{\text{Cd}}^{(\alpha)}} \delta_{0,m}^{\text{Cd},\gamma} + \frac{\Delta M_{\text{H}}^{(\alpha)}}{M_{\text{H}}^{(\alpha)}} \delta_{0,m}^{\text{H},\gamma} \right\} \left(\frac{\mu_1}{\mu_\alpha} \right)^m$

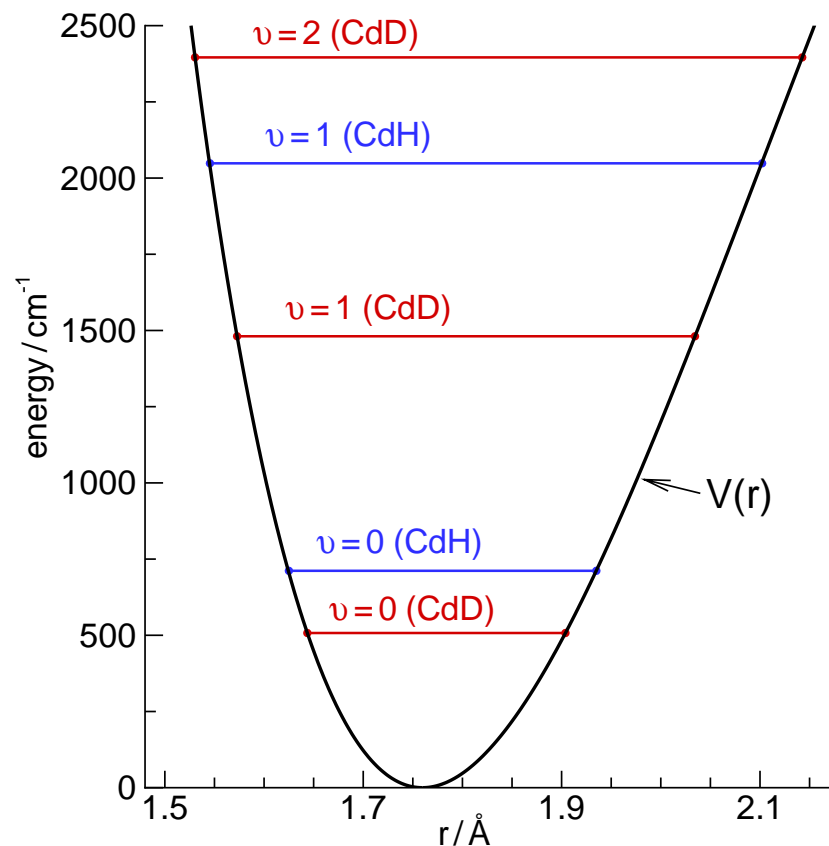
What was the problem?

Since the data considered involved only pure rotational transitions with $v = 0$, the analysis treated the rotational and spin-rotation splitting parameters as being *independent of v* !!
e.g.,

$$B_{v=0}(^{114}\text{Cd D}) = B_{v=0}(^{114}\text{Cd H}) \frac{\mu(^{114}\text{Cd H})}{\mu(^{114}\text{Cd D})}$$

... and the solution?

Even if only $v = 0$ data are considered, a combined treatment of multiple isotopomers effectively introduces v -dependence, so we should *allow for v -dependent rotational and spin-orbit splitting parameters!*



A fit to only the far-IR pure rotational data for $v = 0$ levels of 6 isotopomers of both CdH and CdD gives physically realistic $Y_{1,1} = \alpha_e$ values.

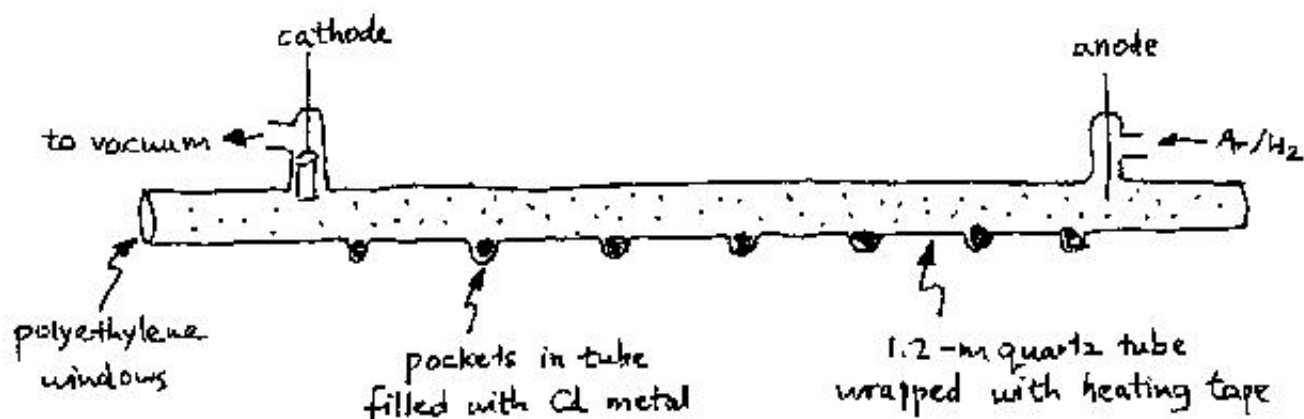
$^{114}\text{Cd } ^1\text{H}$ parameter [cm $^{-1}$]	only $v=0$ far-IR data		only $v=0 - 2$ mid-IR data Jones & co-workers	all $v=0 - 2$ mid- & far-IR data present
	Varberg & Roberts	present		
$Y_{0,1}$	5.325411 (1)	5.442 (1)	5.44073 (12)	5.44676 (4)
$Y_{1,1}$	—	−0.233 (2)	−0.22071 (13)	−0.2409 (1)
$10^4 Y_{0,2}$	−3.1709 (1)	−3.0934 (1)	−3.101 (2)	−3.126 (2)
$10^4 Y_{1,2}$	—	−0.1559 (3)	−0.076 (6)	−0.032 (6)
number of data	214	214	479	749
No. of non-HF parameters	19	16	19	31
DRMSD = $\overline{\text{dd}}$	1.61	1.71	2.1	1.52

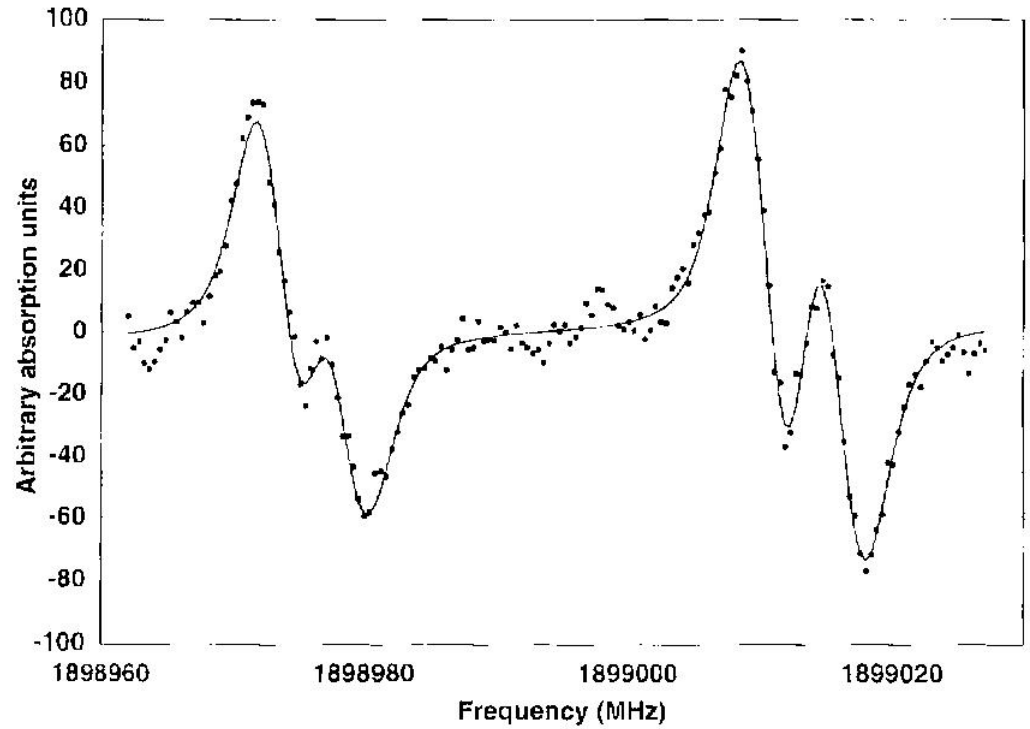
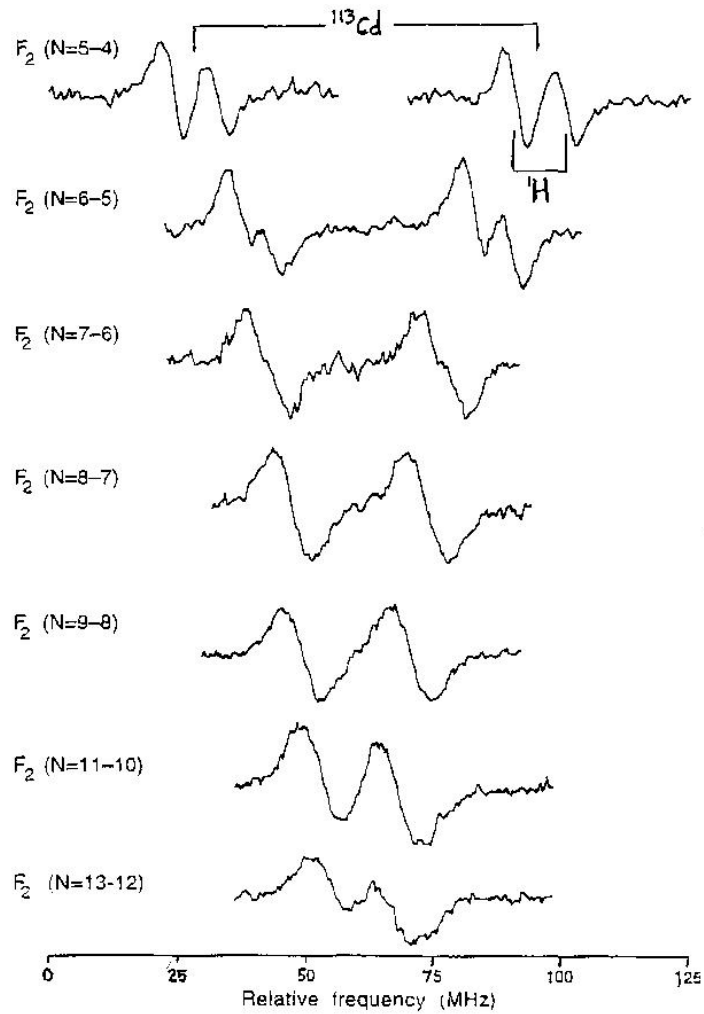
Conclude:

- A combined-isotopomer fit to pure rotational data for $v=0$ for hydrides and deuterides should allow for v -dependence of the band-constant parameters!
- If this v -dependence is neglected, achieving good fits to high quality data may require introduction of spurious non-physical parameters.

New Far-IR Data for 8 Isotopomers of $v=1$ CdH & CdD

- Tunable far-IR radiation is generated by mixing light from two frequency-stabilized CO₂ lasers with a tunable microwave amplifier
- Detector is a liquid-helium-cooled bolometer
- CdH or CdD generated in a discharge tube. Cd is placed in small depressions equally spaced along the tube which is wrapped with heating tape and heated to about 480°C. A positive column discharge (current 100 mA) is maintained as H₂ (at ~ 0.4 Torr) or D₂ (20% D₂ in Ar at ~ 0.7 Torr) flows through the tube.





Use known hyperfine parameters to determine “hyperfine-free” far-IR transition energies, and fit all data to the model:

$$\begin{aligned}
 E_{v,J}^{(\alpha)} = & \sum_m \sum_l \left\{ Y_{l,m}^{(1)} + \frac{\Delta M_{\text{Cd}}^{(\alpha)}}{M_{\text{Cd}}^{(\alpha)}} \delta_{l,m}^{\text{Cd}} + \frac{\Delta M_{\text{H}}^{(\alpha)}}{M_{\text{H}}^{(\alpha)}} \delta_{l,m}^{\text{H}} \right\} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \tfrac{1}{2})^l [N(N+1)]^m \\
 & + \begin{cases} \frac{1}{2} N \sum_m \sum_l \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \tfrac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N + \tfrac{1}{2} \\ -\frac{1}{2} (N+1) \sum_m \sum_l \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \tfrac{1}{2})^l [N(N+1)]^{m-1} & \text{for } J = N - \tfrac{1}{2} \end{cases}
 \end{aligned}$$

Performing a combined-isotomomer fit

- to 275 far-IR data for 12 isotopomers with hyperfine splittings removed using parameters from single-isotopomer analyses: typical uncertainties $\pm 0.000\,005\text{ cm}^{-1}$
- plus 470 mid-IR data for 14 isotopomers: estimated uncertainties $\pm 0.001\text{ cm}^{-1}$,
- yielding a “*dimensionless RMS deviation*” of $\overline{\text{d}\text{d}} = 1.52$.

yields the parameters (all in units cm^{-1}) presented below.

	“mechanical”	B-O breakdown		spin-rotation	
$Y_{1,0}$	1443.405 (5)	$\delta_{1,0}^{\text{H}}$	1.059 (2)		
$Y_{2,0}$	−48.359 (4)				
$Y_{3,0}$	−3.0222 (9)	$\delta_{0,1}^{\text{Cd}}$	$4.83 (7) \times 10^{-5}$		
$Y_{0,1}$	5.44676 (4)	$\delta_{0,1}^{\text{H}}$	$4.67 (3) \times 10^{-3}$	$\gamma_{0,1}$	0.62941 (2)
$Y_{1,1}$	−0.2409 (1)	$\delta_{1,1}^{\text{H}}$	$7.8 (6) \times 10^{-4}$	$\gamma_{1,1}$	−0.04970 (9)
$Y_{2,1}$	$−5.09 (8) \times 10^{-3}$			$\gamma_{2,1}$	$3. (1) \times 10^{-4}$
$Y_{3,1}$	$−3.42 (2) \times 10^{-3}$			$\gamma_{3,1}$	$−10.0 (6) \times 10^{-4}$
$Y_{0,2}$	$−3.126 (2) \times 10^{-4}$	$\delta_{0,2}^{\text{H}}$	$1.9 (2) \times 10^{-6}$	$\gamma_{0,2}$	$−1.6888 (9) \times 10^{-4}$
$Y_{1,2}$	$−3.2 (6) \times 10^{-6}$	$\delta_{1,2}^{\text{H}}$	$−3.0 (4) \times 10^{-6}$	$\gamma_{1,2}$	$−4.8 (2) \times 10^{-6}$
$Y_{2,2}$	$−11.2 (3) \times 10^{-6}$			$\gamma_{2,2}$	$−2.44 (6) \times 10^{-6}$
$Y_{0,3}$	$3.34 (7) \times 10^{-9}$	$\delta_{0,3}^{\text{H}}$	$−9.2 (2) \times 10^{-10}$	$\gamma_{0,3}$	$9.6 (3) \times 10^{-9}$
$Y_{1,3}$	$−9.25 (16) \times 10^{-9}$			$\gamma_{1,3}$	$−4.5 (6) \times 10^{-9}$
$Y_{0,4}$	$−8. (2) \times 10^{-13}$			$\gamma_{0,4}$	$−2.2 (6) \times 10^{-12}$
$Y_{1,4}$	$−3.6 (4) \times 10^{-12}$				

Future Work:

- Resolve problems with a few of the $v = 1$ pure rotation CdD data.
- Combine the mid- and far-IR data with electronic spectral data to generate a more comprehensive unified description of this system.