5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Examination #1
Due April 14, 1978

This is an open book, open note, unlimited time examination. I expect that you will not discuss or compare your answers to these questions with anyone currently enrolled in 5.76.

I. Dreckium Monoxide

Dreckium is a superheavy element which belongs in Group IIA of the periodic table. It has atomic number 120 and there are two isotopic species ^{324}Dk and ^{326}Dk with atomic weights 324.00 and 326.00 and relative abundance 95% and 5%. Recently, spectra of DkO have been reported.

A. Microwave Spectrum (Recorded at $T = 1500$K)

Microwave spectra have been obtained in the K_u ($12 - 18$ GHz), K_a ($26 - 36$ GHz), and Q ($33 - 50$ GHz) band regions. The following transitions and their relative intensities are observed:

ν (MHz)	Intensity
16560.08	100
16555.30	5
16524.42	50
16519.66	3
16488.76	30
16484.02	1
33120.04	100
33110.48	5
33048.72	50
33039.20	3
32977.40	30
32967.92	1
49679.76	100
49665.42	5
49572.78	50
49558.50	3
49465.80	30
49451.58	1

It is not meaningful to compare relative intensities of widely separated lines. An extensive search of the regions near 8250 MHz and 24700 MHz yielded no additional lines.

B. Infrared Spectrum

Several bands were observed and the following vibrational constants for the ground state were obtained:

	$^{324}\text{Dk}^{16}\text{O}$	$^{326}\text{Dk}^{16}\text{O}$
ω_e	710.17 cm^{-1}	710.07
$\omega_e x_e$	1.02	1.02

C. Electronic Spectrum

One band in the electronic absorption spectrum was recorded in which a head formed near 4387 Å. It was believed that lines of comparable intensity separated by 0.03 cm^{-1} could have been resolved. The band was not rotationally analyzed because, although it appeared to be part of the $A^1\Pi - X^1\Sigma^+$ band system, the computer automated assignment procedure was rendered ineffective by perturbations.

The following lines and relative intensities were observed:

22794.48 cm^{-1}	2	84.13	3	67.24	3
94.40	4	83.63	1	67.01	2
94.16	4	83.10	5	66.44	2
93.75	4	83.05	11	65.99	8
93.62	2	82.75	2	64.53	1
93.29	4	82.46	2	64.25	3
93.20	4	81.40	1	63.90	2
92.81	5	81.12	16	62.90	7
92.49	7	81.02	3	62.07	1
92.16	7	80.02	1	61.08	5
91.63	8	79.30	3	59.66	6
91.34	8	79.00	16	59.59	1
90.61	8	78.58	0	57.99	3
90.37	9	77.32	3	57.78	2
89.48	5	76.78	5	57.05	0
89.42	4	76.72	10	56.24	5
89.23	10	75.09	3	54.66	3
88.23	5	74.43	5	54.29	2
88.08	4	74.28	9	52.66	5
87.93	10	72.66	4	51.13	3
86.89	4	71.98	4	48.93	4
86.57	5	71.68	9	47.40	2
86.46	11	70.78	1	45.03	4
85.50	3	70.04	3	43.49	2
84.91	5	69.48	3	40.97	3
84.84	11	68.92	8	39.41	2
84.58	1	68.72	1	35.15	2
				30.73	1

In an effort to understand the peturbed band, a low resolution absorption spectrum of Dk^{18}O was

recorded. Four red degraded bands were observed in the isotopic spectrum near 4387 Å:

$$
\begin{array}{lll}
22675.51 \text{ cm}^{-1} & A^1\Pi - X^1\Sigma^+ & (v'_\Pi, v'' = 0) \\
22706.55 & B^1\Sigma^+ - X^1\Sigma^+ & (v'_{\Sigma'}, v'' = 0) \\
23110.51 & A - X & (v'_\Pi + 1, v'' = 0) \\
23201.77 & B - X & (v'_\Sigma + 1, v'' = 0)
\end{array}
$$

All four of these bands appear to be free of perturbations and the two B−X bands are much weaker than the A−X bands.

1. a. (5 points) Assign the microwave spectrum.

    b. (5 points) Determine B_e, α_e, D_e, and r_e for ^{324}Dk^{16}O and ^{326}Dk^{16}O.

    c. (5 points) Use the Kratzer relation to estimate ω_e for ^{324}Dk^{16}O:

    $$D_e = 4B_e^3 \big/ \omega_e^2.$$

    Now use the Pekeris relation to estimate $\omega_e x_e$ for ^{324}Dk^{16}O:

    $$\alpha_e = \frac{6}{\omega_e}\left[\left(\omega_e x_e B_e^3\right)^{1/2} - B_e^2\right].$$

2. a. (20 points) Rotationally analyze the 4387 Å band.

    [HINT: 82 lines are too many to attempt to assign without a specific plan of attack. I suggest the following:

    (i) Prepare a **long** ($\sim 1''$ per cm^{-1}) stick spectrum. Represent the relative intensities as stick heights. Be sure to leave about $1''$ of space above and below your stick spectrum. You will use this space to organize the lines into branches using a "railroad tie" diagram.

    (ii) Prepare another **long** strip of graph paper using **exactly** the same length per cm^{-1} scale. Plot ground state combination differences,

    $$\Delta_2 F(J'') = B''(4J'' + 2) - D''(8J^3 + 12J^2 + 12J + 4),$$

    determined from the microwave constants. Before making separate strips for several v'' levels, do some spot checking to determine the v'' assignment for the band. You are going to use this strip as a ruler to find $P(J+1)$ and $R(J-1)$ lines connected to a common J′ level. The zero of the strip is placed on top of the $P(J+1)$ line and the J'th combination difference mark will then fall on top of the $R(J-1)$ line. $P(J+1)$ is always to the red of $R(J-1)$. Lines in a branch vary smoothly in intensity (unless two lines accidentally fall on top of each other) and the separation of consecutive members of a branch varies smoothly (except at some perturbations):

(iii) Prepare the "railroad tie" diagram. As you recognize lines connected with a common upper level with known J', mark these lines as follows:
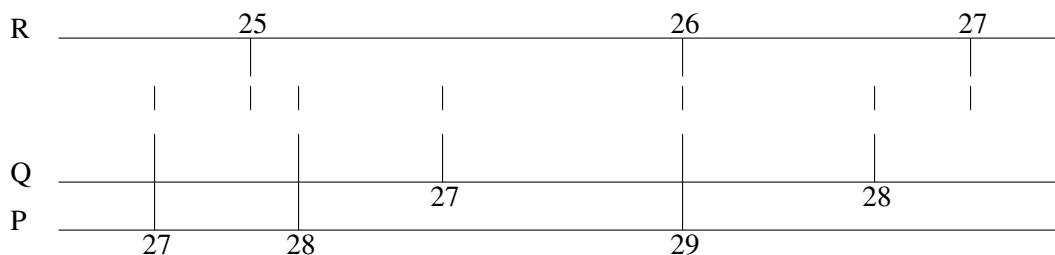
This should permit you to identify **every** line in the above list. Note that, at perturbations, there may be more than one upper level with a given J' value.

END OF HINT.]

b. (10 points) Obtain band origins and B values for the $A^1\Pi$ and perturbing $B^1\Sigma^+$ state. The easiest way to do this is by some sort of graphical method. Recall that in a $^1\Pi \sim {}^1\Sigma^+$ perturbation, the $^1\Pi$ f–levels are not affected by the perturbation. The perturbation matrix element,

$$\left\langle {}^1\Pi_e|\mathbf{H}|^1\Sigma^+ \right\rangle = \beta \left\langle v_\Pi|B|v_\Sigma \right\rangle [2J(J+1)]^{1/2},$$

is J–dependent. It will be necessary to convert observed **transition frequencies** into term energies (energies of the J' level above $v'' = 0$, $J'' = 0$) by adding to the transition frequency a suitable ground state rotational energy. You will need to prepare a table of such ground state rotational energies (perhaps at the same time that you are preparing your table of $\Delta_2 F(J'')$ values).

c. (5 points) Describe how you know whether the perturbation involves the upper or lower electronic state. What is the magnitude of the rotationless part of the perturbation matrix element,

$$\beta \left\langle v_\Pi|B|v_\Sigma \right\rangle?$$

What determines the relative intensities of main and extra lines?

d. (10 points) Use the isotope shift information to obtain vibrational assignments of the $A^1\Pi$ and perturbing level. You do **not** have sufficient information to determine both ω_e and $\omega_e x_e$; you will have to **guess** a reasonable value for $\omega_e x_e$.

II. Effective Hamiltonian Matrices.

    A. Set up the Hamiltonian,

$$\mathbf{H} = \mathbf{H}^{\text{ROT}} + \mathbf{H}^{\text{SPIN-ORBIT}}$$

    for the 9 basis functions:

	Λ	S	Σ	Ω	
$^3\Pi$	1	1	1	2	$\left\vert^3\Pi_2\right\rangle\left\vert v_\Pi\right\rangle$
	-1	1	-1	-2	$\left\vert^3\Pi_{-2}\right\rangle\left\vert v_\Pi\right\rangle$
	1	1	0	1	$\left\vert^3\Pi_1\right\rangle\left\vert v_\Pi\right\rangle$
	-1	1	0	-1	$\left\vert^3\Pi_{-1}\right\rangle\left\vert v_\Pi\right\rangle$
	1	1	-1	$+0$	$\left\vert^3\Pi_0\right\rangle\left\vert v_\Pi\right\rangle$
	-1	1	1	-0	$\left\vert^3\Pi_{-0}\right\rangle\left\vert v_\Pi\right\rangle$
$^3\Sigma^+$	0	1	1	1	$\left\vert^3\Sigma_1^+\right\rangle\left\vert v_\Sigma\right\rangle$
	0	1	0	0	$\left\vert^3\Sigma_0^+\right\rangle\left\vert v_\Sigma\right\rangle$
	0	1	-1	-1	$\left\vert^3\Sigma_{-1}^+\right\rangle\left\vert v_\Sigma\right\rangle .$

    Let

$$\alpha \equiv \langle\Lambda = 1\|A\mathbf{L}_+\|\Lambda = 0\rangle$$

$$\beta \equiv \langle\Lambda = 1\|\mathbf{L}_+\|\Lambda = 0\rangle$$

    and use

$$\langle 1|\mathbf{H}|2\rangle = (-1)^{2J+S_1+S_2+\sigma_1+\sigma_2}\langle -1|\mathbf{H}|-2\rangle$$

    where $\sigma = 1$ for Σ^- states and 0 for all other states, to ensure phase consistency for

$$\langle\Lambda = 1|\mathbf{H}|\Lambda = 0\rangle \ \text{and} \ \langle\Lambda = -1|\mathbf{H}|\Lambda = 0\rangle$$

    matrix elements.

    B. Construct the e/f parity basis using the following phase definitions

$$\sigma_v|v, n\Lambda^\sigma S\Sigma, \Omega JM\rangle = (-1)^{J-2\Sigma+S+\sigma}|v, n-\Lambda^\sigma S-\Sigma, -\Omega JM\rangle$$

    e-levels $\sigma_v\psi = +(-1)^J\psi$

    f-levels $\sigma_v\psi = -(-1)^J\psi.$

    C. Factor the 9×9 Hamiltonian into a 5×5 and a 4×4 matrix using the e/f basis functions.

    D. Obtain the centrifugal distortion correction terms for the $\left\langle^3\Pi_0|\mathbf{H}|^3\Pi_0\right\rangle_e$, $\left\langle^3\Pi_1|\mathbf{H}|^3\Pi_1\right\rangle_e$, and $\left\langle^3\Pi_1|\mathbf{H}|^3\Pi_0\right\rangle_e$
    matrix elements.

$$D_\Pi \equiv -\sum_{v_{\Pi'}}\frac{\left\langle v_\Pi|B|v_\Pi'\right\rangle^2}{E_{\Pi_v}^0 - E_{\Pi_{v'}}^0}.$$

E. Obtain the correction terms for the effect of remote $^3\Sigma^+$ levels on $^3\Pi$ for the $\left\langle {}^3\Pi_0 |\mathbf{H}| {}^3\Pi_0 \right\rangle_{e \text{ and } f}$ and $\left\langle {}^3\Pi_1 |\mathbf{H}| {}^3\Pi_1 \right\rangle_{e \text{ and } f}$ matrix elements.

$$o \equiv \sum_{v'_\Sigma} \frac{\left[\frac{1}{2}\alpha \left\langle v_\Pi | v'_\Sigma \right\rangle\right]^2}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

$$p \equiv 4 \sum_{v'_\Sigma} \frac{\left[\frac{1}{2}\alpha\beta \left\langle v_\Pi | v'_\Sigma \right\rangle \left\langle v_\Pi | B | v'_\Sigma \right\rangle\right]}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

$$q \equiv 2 \sum_{v'_\Sigma} \frac{\left[\beta \left\langle v_\Pi | B | v'_\Sigma \right\rangle\right]^2}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

Express diagonal contributions to the Λ–doubling of the $\Omega = 0$ and 1 $^3\Pi$ substates in terms of o, p, and q.