5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

**Examination #2**

Following is a complete list of observed transitions involving levels $J = 0, 1$, and 2 for two isotopomers of formaldehyde in their vibrational ground states:

$$H_2{}^{12}C^{16}O \qquad H_2{}^{13}C^{16}O$$

| $H_2{}^{12}C^{16}O$ | $H_2{}^{13}C^{16}O$ |
|---|---|
| 71.14 MHz | — |
| 4829.66 | 4593.09 |
| 14488.65 | 13778.86 |
| 72837.97 | 71024.80 |
| 140839.54 | 137449.97 |
| 145602.98 | 141983.75 |
| 150498.36 | 146635.69 |

Note that in a real spectrum you could not arrange to see only transitions involving $J = 0, 1$, and 2. In fact, there are more than 54 observed $H_2{}^{12}C^{16}O$ transitions below 150498.36 MHz.

I. (50 points) Assign the above microwave transitions for both isotopic molecules. It is distinctly to your advantage to assume that $H_2CO$ belongs to the $C_{2v}$ point group and then show that the observed spectrum is consistent with this assumption. You will find the energy level expressions on the next page (from page 192 of Bernath) to be useful, but I doubt whether the spectrum can be assigned without knowledge of the dipole moment direction relative to the inertial axis system, asymmetric top rotational selection rules, and a good guess of the trial geometry.

II. (10 points) Explain why no other transitions involving $J = 0, 1$, and 2 were observed.

III. (10 points) Obtain values of A, B, and C for the two isotopic species. Since we have neglected centrifugal distortion, it will not be possible to fit all transitions exactly with only 3 rotational constants. Devise a procedure that gives a "best fit" to all lines.

IV. (10 points) Explain why the inertial defect

$$\Delta = I_c - I_a - I_b$$

is a good test for planarity. Why does $H_2CO$ appear NOT to be planar from the microwave spectrum?

V. (20 points) Obtain a best possible geometry for $H_2CO$ using your A, B, and C values for the two isotopomers. If you have not yet discovered the value of iterative calculations on a pocket calculator, now is the time!

| $J_{K_a,K_c}$ | Rotational energy |
|---|---|
| $0_{00}$ | $0$ |
| $1_{10}$ | $A + B$ |
| $1_{11}$ | $A + C$ |
| $1_{01}$ | $B + C$ |
| $2_{20}$ | $2A + 2B + 2C + 2\sqrt{(B-C)^2 + (A-C)(A-B)}$ |
| $2_{21}$ | $4A + B + C$ |
| $2_{11}$ | $A + 4B + C$ |
| $2_{12}$ | $A + B + 4C$ |
| $2_{02}$ | $2A + 2B + 2C - 2\sqrt{(B-C)^2 + (A-C)(A-B)}$ |
| $3_{30}$ | $5A + 5B + 2C + 2\sqrt{4(A-B)^2 + (A-C)(B-C)}$ |
| $3_{31}$ | $5A + 2B + 5C + 2\sqrt{4(A-C)^2 - (A-B)(B-C)}$ |
| $3_{21}$ | $2A + 5B + 5C + 2\sqrt{4(B-C)^2 + (A-B)(A-C)}$ |
| $3_{22}$ | $4A + 4B + 4C$ |
| $3_{12}$ | $5A + 5B + 2C - 2\sqrt{4(A-B)^2 + (A-C)(B-C)}$ |
| $3_{13}$ | $5A + 2B + 5C - 2\sqrt{4(A-C)^2 - (A-B)(B-C)}$ |
| $3_{03}$ | $2A + 5B + 5C - 2\sqrt{4(B-C)^2 + (A-B)(A-C)}$ |