Advanced Chemistry Classroom and Laboratory ——————————

Cometary Spectroscopy for Advanced Undergraduates

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Comets have always generated interest among both the general public and the scientific community. Public interest ranges from that of the casual comet observer to that of the amateur astronomer who continuously searches for new and undiscovered comets. One superstitious stigma historically associated with comets is, unfortunately, the belief that comets are a sign of a natural catastrophe or some sort of spiritual omen of events to come. In 1910, a headline to an article in *The New York Times* read "Chicago is Terrified—Women Are Stopping Up Doors and Windows to Keep Out Cyanogen" in reference to Comet Halley's appearance during that year. More recently, the mass suicide by the members of the Heaven's Gate cult in San Diego, who interpreted the appearance of Comet Hale–Bopp as a sign of leaving this existence for the "next level", is another indication of the impact of comets on society.

The interest of the scientific community in comets stems from a different source. Comets are believed to be relics of our solar system. By studying them, scientists hope to understand the chemical and physical conditions during the formation and evolution of our solar system. For interesting reading on comets and their origin, the reader is referred to refs *1–3* and references therein.

We briefly mentioned Comet Hale–Bopp above. This comet, which reached perihelion (closest distance to the sun) on April 1, 1997, put on a spectacular show in the months of March and April of that year. In 1996, Comet Hyakutake,

although not as bright as Hale–Bopp, displayed a similar spectacle. These comets, like all other observed comets, appear visible because they reflect, absorb, and emit radiation. In fact, the frequency range of electromagnetic radiation observed from comets spans the X-ray, UV, visible, IR, microwave, and radio frequencies. Scientists have used this fact as a tool in studying the chemical composition of comets. Because atoms and molecules absorb and emit electromagnetic radiation at well-defined and discrete wavelengths, scientists studying the radiation collected from comets have been able to determine the presence of many chemical species. Some of the species observed in comets are H, C, O, Na, C_2, OH, CH, CO, CS, NH, NH_2, and H_2O. Since most of these species are reactive and hence chemically unstable, they are thought to be formed from the photodissociation of stable parent molecules. Some possible parent molecules for these species are H_2O, CO_2, CO, HCN, CS_2, C_2H_2, and NH_3; and in a recent paper, Sorkhabi et al. showed that C_2H_2 is the major source of C_2 in comet Hyakutake (*4*).

It is clear that deciphering the information contained in the collected radiation from a comet requires knowledge of spectroscopy. Therefore, an intimate relationship exists between astronomy and spectroscopy. We believe that it is worthwhile to expose students of advanced physical chemistry courses to topics in astrochemistry/astrophysics, such as cometary observations. In this paper, we attempt to do this. We first discuss spectral band intensities. Then we introduce a simple model for predicting band intensities in comets. We will limit our discussion only to vibrational electronic (vibronic) transitions and apply our model to the observed vibronic bands of carbon monosulfide (CS) in the Hubble space telescope (HST) spectrum of Comet Hyakutake.

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Band Intensities and Franck–Condon Factors

For electronic transitions of diatomic molecules, such as CS, the transition probability (emission or absorption) is proportional to the square of the transition moment, R:

$$R = \int_0^\infty \psi'(r)\hat{\mu}\psi''(r)dr \qquad (1)$$

$\psi'(r)$ and $\psi''(r)$ are the total wave functions of the upper and lower states, respectively, r is the internuclear separation, and μ is the dipole moment operator. Throughout this paper, we will refer to the upper state by using a single prime and to the lower state by using a double prime. Transition probabilities play a central role in spectroscopy for they are one of the main factors that determine intensities in measured spectra. A measured spectrum is usually presented as a plot of intensity versus wavelength, such as the one shown in Figure 1. The intensity, I, is directly proportional to the product of the square of the transition moment, R, and the population of the initial state, Q,

$$I = C_1 Q |R|^2 \qquad (2)$$

where C_1 is a proportionality constant. Equation 2 is an indispensable tool for spectroscopists in the analysis of intensity distributions. For example, if R and Q are known, eq 2 can be used to predict intensities for transitions of interest or, knowing I and R, the populations can be determined from the observed bands in a measured spectrum. As we will see below, C_1 need not be known explicitly if the appropriate system and appropriate set of calculations are chosen. At first glance, this exercise appears trivial. However, determining R—or more specifically, evaluation of the integral in eq 1—is not a trivial task and it is, therefore, common practice to simplify this integral by making some approximations.

For a description of deriving the Franck–Condon principle from Born–Oppenheimer approximation, see refs 5–7. It can be shown that

$$I = C_1 Q \left| \overline{R}_e p(v',v'') \right|^2 = C_1 Q \left| \overline{R}_e \right|^2 q(v',v'') \qquad (3)$$

where $q(v',v'')$ is the Franck–Condon factor, $p(v',v'')$ is the vibrational overlap integral, and $\overline{R}_e$ is an averaged value of the transition moment (electronic matrix element).

To predict I for a given transition or to determine Q for a given state using the spectroscopic intensity, we need $\overline{R}_e$ and $q(v',v'')$. $\overline{R}_e$ can be either calculated or determined experimentally. An accurate calculation of $\overline{R}_e$ is beyond the scope of this paper; nonetheless, it can be determined by using the following formula (8):

$$\left| \overline{R}_e \right|^2 = C_2 f_{osc} = C_2 \left(\frac{1.50}{\overline{\nu}^2} \frac{1}{\tau} \frac{g'}{g''} \right) \qquad (4)$$

where f_{osc} is the oscillator strength for the electronic transition of interest, $\overline{\nu}$ is the energy of the transition in cm^{-1}, τ is the lifetime of the upper state, g' is the degeneracy of the upper electronic state, g'' is the degeneracy of the lower electronic state, and C_2 is a proportionality constant. This approximation holds for the case of X–A electronic transitions such as the one described below (i.e., the CS ($X\,^1\Sigma$–$A\,^1\Pi$)
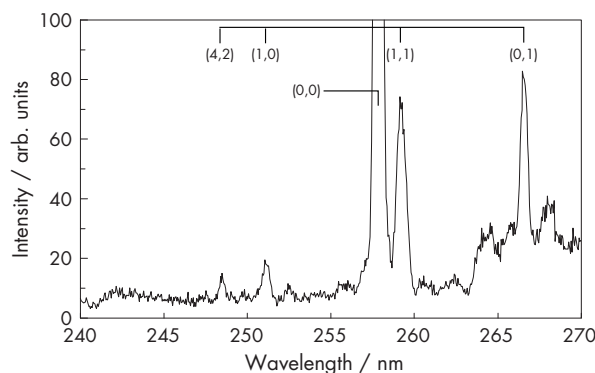

Figure 1. Part of the Hubble space telescope spectrum of Comet Hyakutake. The wavelength region shown contains primarily vibronic bands of the CS ($X\,^1\Sigma$ - $A\,^1\Pi$) system. We have assigned the (4,2), (1,0), (0,0), (1,1), and (0,1) vibronic bands of this system. Notice that the (0,0) band is much stronger than the other bands and goes off scale. We reduced the scale to show all the features of the spectrum.

system). Substituting for $|\overline{R}_e|^2$, eq 3 becomes

$$I = C_1 C_2 Q\, q(v',v'') \left(\frac{1.50}{\overline{\nu}^2} \frac{1}{\tau} \frac{g'}{g''} \right) \qquad (5)$$

Determination of g'', g', τ, and $\overline{\nu}$ is either trivial or the value can be obtained from the literature. Unfortunately, calculation of overlap integrals and Franck–Condon factors is not as trivial, and we will now show how to calculate $p(v',v'')$ and $q(v',v'')$.

To calculate $q(v',v'')$, vibrational wave functions for the upper and lower states of a transition are needed. These wave functions can be obtained by solving the Schrödinger equation with some suitable potential energy term in the Hamiltonian operator. For a diatomic molecule, the Morse function, $U(r)$, is commonly used to describe the potential energy between the two nuclei as a function of the internuclear separation. It is given by the expression

$$U^j(r) = D^j[1 - e^{-\alpha^j(r-r_e^j)}]^2 \qquad (6)$$

where D^j is the dissociation energy of the jth electronic state, r_e is the equilibrium bond length, and

$$\alpha^j = \left[\frac{4\pi c \mu \omega_e x_e^j}{\hbar} \right]^{1/2} \qquad (7)$$

Equations 6 and 7 are provided for the consistency of notation between the equations that follow and those found in the literature. In a previous paper (9), we calculated potential energy curves using a variety of methods and noted that the Morse function does a reasonably good job in comparison with more sophisticated methods. By using $U^j(r)$ as the potential energy in the Hamiltonian and solving the Schrödinger equation, one can obtain the vibrational wave functions for the jth electronic state of the diatomic molecule. Fraser and Jarmain (10–11) used this approach to determine the vibrational wave functions, ψ_v' and ψ_v''. They then derived analytical expressions for the overlap integrals, $p(v',v'')$. Here we provide their equations for calculating $p(0,0)$, $p(0,1)$,

$p(1,0)$, and $p(1,1)$. A few mistakes were found in their equations, which have been corrected here. The overlap integral $p(0,0)$ can be calculated using

$$p(0,0) = \exp\left[-\left\langle \frac{(\Delta\Omega)^2}{2}\left[\frac{1}{(\Omega-1)} + \frac{1}{2(\Omega-1)^2}\right] + \frac{(\Delta\Omega)^4}{12}\frac{1}{(\Omega-1)^3} + \frac{1}{2}(\Omega-1)\left(\delta^2 + \frac{1}{2}\delta^4\right) + (\Delta\Omega)\left(\delta + \frac{1}{3}\delta^3\right)\right\rangle\right] \quad (8)$$

where the terms Ω, $\Delta\Omega$, and δ are defined as

$$\Omega = \frac{1}{2}(\Omega'' + \Omega'); \quad \Delta\Omega = \frac{1}{2}(\Omega'' - \Omega'); \quad \delta = 1 - \frac{1}{P''} = \frac{1}{P'} - 1$$

and

$$K^j = \frac{(\omega_e)^j}{(\omega_e x_e)^j}; \quad \Omega^j = K^j(\alpha^j/\alpha)^2; \quad \lambda^j = \Omega^j e^{\alpha r_e^j}$$

$$\lambda = \frac{1}{2}(\lambda'' + \lambda'); \quad P^j \equiv \frac{\lambda}{\lambda^j}; \quad \alpha = \frac{1}{2}(\alpha'' + \alpha')$$

where $j = '$ or $''$ and the primes refer to the upper and lower electronic states, respectively. All these terms can be calculated from the molecular constants ω_e, $\omega_e x_e$, r_e, and μ for a diatomic molecule in a given electronic state. Molecular constants for a large collection of diatomic molecules can be found in ref *12*. Once $p(0,0)$ is determined, $p(1,0)$ can be calculated from the following expression:

$$\frac{p(1,0)}{p(0,0)} = \left|\frac{N'(1)}{N''(0)}P'\left\{\frac{\Delta\Omega}{\Omega-2} + \delta\right\}\right| \quad (9)$$

Changing the prime to double prime and vice versa in eq 9 gives the ratio $p(0,1)/p(0,0)$. To get the value for the overlap integrals, $p(1,0)$ and $p(0,1)$, one simply multiplies these ratios by $p(0,0)$. Similarly, the value for $p(1,1)$ can be calculated using

$$\frac{p(1,1)}{p(0,0)} = \left|\frac{N''(1)N'(1)}{N''(0)N'(0)}\left\langle 1 - \left[P''\frac{(\Omega''-2)}{(\Omega-2)} + P'\frac{(\Omega'-2)}{(\Omega-2)} + P''P'\frac{(\Omega''-2)(K_2'-2)}{(\Omega-2)(\Omega-3)}\right]\right\rangle\right| \quad (10)$$

Here the terms $N^j(v)$ are the normalization constants and can be determined by the general equation

$$\frac{N^j(v)}{N^j(v-1)} = \left[\frac{(\Omega^j-v)}{v}\frac{(\Omega^j-2v-1)}{(\Omega^j-2v+1)}\right]^{1/2} \quad (11)$$

We have calculated Franck–Condon factors for the CS ($X\,^1\Sigma$–$A\,^1\Pi$) system using the above equations. The results are shown in Table 1. Using eqs 7 through 11, $q(v',v'')$ can be calculated; thus, the only unknowns for the evaluation of I, using eq 5, are C_1, C_2, and Q, the population of the initial state involved in a transition. Here we will use a Boltzmann distribution to approximate Q. As we will see below, one can avoid using C_1 and C_2 by calculating intensity ratios, for which case these constants cancel out.

A Simple Model for the Prediction of Band Intensities in Comets

We can now use the above equations to predict intensity ratios in the UV–vis cometary emission spectra. A good system for this purpose is the carbon monosulfide, CS, ($X\,^1\Sigma$–$A\,^1\Pi$) system. Figure 1 shows part of the Hubble space telescope emission spectrum of Comet Hyakutake. In the HST spectrum, emission bands of many diatomic molecules are present, among which are several bands of the CS ($X\,^1\Sigma$–$A\,^1\Pi$) system.

The origin of these emission bands is made clear in the schematic diagrams shown in Figure 2. Transitions shown in the figure are called vibronic transitions because they involve transitions from a vibrational level of one electronic state to a vibrational level of another electronic state. Vibronic bands are labeled by the notation (v',v''). For example, $(2,0)$ refers to a transition involving $v' = 2$ of the upper electronic state and $v'' = 0$ of the lower electronic state. In Figure 2, two electronic states of CS, $X\,^1\Sigma$ and $A\,^1\Pi$, are shown with their respective vibrational states. Also shown is the excitation of the CS molecule from $v'' = 1$ of the $X\,^1\Sigma$ state to $v' = 2$ of the $A\,^1\Pi$ state. Excitation from any v'' to any v' is allowed; we show only one excitation, for simplicity. Figure 2 also shows emission from $v' = 2$ to several v'' levels. Excitation followed by emission, as shown, constitutes one cycle through the $X\,^1\Sigma$–$A\,^1\Pi$ system. A typical cometary emission spectrum (Fig. 1) involves many cycles—the molecule is excited by absorption of a solar photon and then relaxes to the lower state by emitting a photon, and this process of absorption and emission occurs again and again. We will consider only one cycle in our calculations and assume that the change in the initial population (in the $X\,^1\Sigma$ state) brought about by many subsequent cycles is given by a Boltzmann distribution. As we will show, this simplification actually provides physical insight, for it allows us to derive a vibrational temperature, $T_{v''}$, for CS in the comet.

Table 1. Calculated Franck–Condon Factors for CS ($X\,^1\Sigma$–$A\,^1\Pi$) System

v'/v''	0	1
0	0.778	0.189
1	0.200	0.422

NOTE: For the $X\,^1\Sigma$ state, $r_e = 1.534$ Å, $\omega_e = 1285.1$ cm^{-1}, and $\omega_e x_e = 5.4$ cm^{-1}. For the A $^1\Pi$ state, $r_e = 1.573$ Å, $\omega_e = 1072.3$ cm^{-1}, and $\omega_e x_e = 10.3$ cm^{-1}. All calculated values for $q(v',v'')$ are within 5% of the values reported in ref *18*.
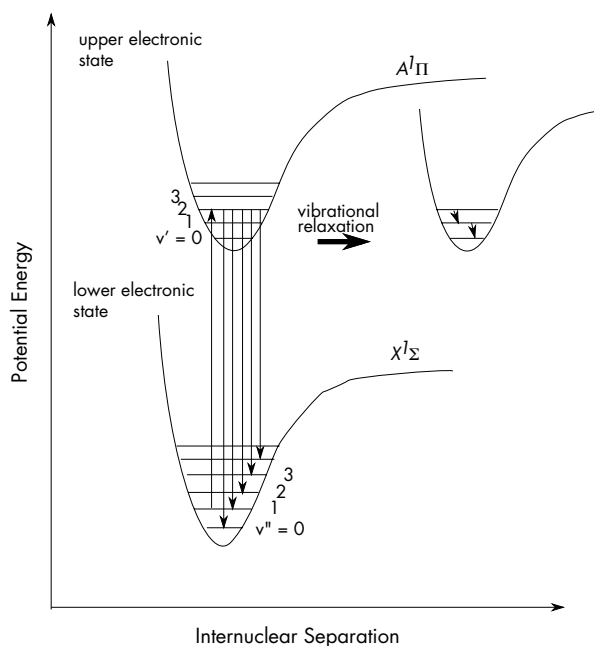
Figure 2. Potential energy curves for the $A\,^1\Pi$ and $X\,^1\Sigma$ electronic states of the CS molecule, with their respective vibrational energy levels. This figure is a pictorial guide to the model discussed in the text. Therefore, the energy gaps between energy levels are not accurate. We show excitation from $v'' = 1$ to $v' = 2$ and emission from $v' = 2$ to $v'' = 0, 1, 2,$ and 3. These transitions are not unique: any combination of transitions (both excitation and emission) is allowed for vibronic transitions. The intensities of these transitions vary and depend heavily on the Franck–Condon factors. Furthermore, excitation can originate from any v'' level and emission can occur from any v' level. Whether these bands are observed will be determined by their transition moment.

The probability of excitation, $P_{\text{excitation}}$, from a vibrational level v'' of a lower electronic state to a vibrational level v' of an upper electronic state is proportional to the product of the oscillator strength, f_{osc}, the solar flux, $F(\lambda)$, the Franck–Condon factor, $q(v',v'')$, and the population of the lower state, $Q_{v''}$, summed over all vibrational levels of the lower electronic states, v'':

$$P_{\text{excitation}} = F(\lambda)\sum_{v''} C_1 C_2 Q_{v''} q(v',v'') f_{\text{osc}} =$$
$$F(\lambda) C_1 C_2 f_{\text{osc}} \sum_{v''} Q_{v''} q(v',v'') \quad (12)$$

Notice the similarity between eq 12 and eq 5. The only difference is the solar flux and the summation over the lower vibrational levels, which takes into account the excitations originating from all the v'' levels. The probability of emission from v' to v'' is proportional to the product of the Franck–Condon factor, the oscillator strength, and the total population in v', $Q_{v'}$:

$$P_{\text{emission}} = C_1 C_2 f_{\text{osc}} Q_{v'} q(v',v'') \quad (13)$$

Therefore, the total probability of observing an emission band in a cometary spectrum is the product of eqs 12 and 13:

$$P_{\text{total}} = C_1^2 C_2^2 F(\lambda) f_{\text{osc}}^2 q(v',v'') \left\{ \sum_{v''} Q_{v''} q(v',v'') \right\}^2 \quad (14)$$

where we have estimated $Q_{v'}$, the population of state v', by

$$\sum_{v''} Q_{v''} q(v',v'')$$

P_{total} is related to the g-factor, a term commonly used among astrophysicists. A discussion of the g-factor will not be presented here, but interested readers are referred to ref 1, pp 100–102.

In Figure 1, emission from CS ($A\,^1\Pi$) is evident. The following bands of the CS ($X\,^1\Sigma$–$A\,^1\Pi$) system were assigned: (0,0), (0,1), (1,0), (1,1), and (4,2). The integrated intensities of these bands from the HST spectrum have been extracted (with the exception of the (4,2) band) relative to the (0,0) band and are reported in Table 2. Table 2 also contains our calculated values of the same ratios using eqs 4 and 8–14. The agreement between observed and calculated values is good for all the ratios.

Excitation to v' of the upper electronic state can originate from many possible v'' levels of the lower electronic state, all of which must be considered. Therefore, the Franck–Condon factors and the oscillator strengths are needed for all of the relevant transitions. Furthermore, the vibrational population distribution in the lower electronic state must be known or approximated. When the observed molecule is formed with high levels of internal excitation, experimental data (if available) can be used. However, caution must be taken to ensure that the observed cometary spectra reflect the nascent internal energy distribution. Laboratory studies of the photodissociation of CS_2 at 193 nm reveal that the CS ($X\,^1\Sigma$) product is formed vibrationally hot (13–15). Since previous studies have suggested that CS is the daughter of CS_2 in comets (16), photodissociation of CS_2 in comets should also lead to vibrationally excited CS. Radiative relaxation of these vibrationally excited CS molecules should occur rapidly because CS has a permanent dipole moment and these transitions are dipole-allowed. This poses a difficulty in determining $Q_{v''}$. Here, $Q_{v''}$ was approximated by using a Boltzmann distribution, which enabled us to use temperature as an adjustable parameter to get the best fit to the data. The ratios given in Table 2 were obtained with a vibrational temperature of 3500 K. This analysis, therefore, provides an estimate, albeit indirect, of the vibrational temperature, and indicates that CS was formed initially with high levels of vibrational excitation and still retained some of its internal excitation at the time of measurement.

Table 2. Values for Intensities of Some Bands of CS ($X\,^1\Sigma$–$A\,^1\Pi$) System

(v'/v'')	From Our Calculations	From Our HST Observations
(0,0)	1	1
(0,1)	0.29	0.37 ± 0.13
(1,1)	0.21	0.28 ± 0.05
(1,0)	0.084	0.080 ± 0.02

Note: All band intensities were normalized to that of the (0,0) band. A Boltzmann distribution was used to approximate $Q_{v''}$. $T_{v''}$ was varied until the best fit to the data was established. The analysis yielded a vibrational temperature of 3500 K for CS in the X state.

Assignment for the Student

1. Use eqs 8–11 to calculate $q(v',v'')$ for the (0,0), (0,1), (1,0), and (1,1) bands of the CS ($X\,^1\Sigma$–$A\,^1\Pi$) system.

2. With the calculated $q(v',v'')$'s and eqs 4 and 12–14, calculate the intensities of the (0,0), (0,1), (1,0), and (1,1) bands (all normalized to the (0,0) band) of the CS ($X\,^1\Sigma$–$A\,^1\Pi$) system. Note that $T_{v''}$, the characteristic vibrational temperature, is an adjustable parameter in the Boltzmann function to fit the calculated values to the observed ones.

3. Compare the calculated and observed values.

4. Report the value of $T_{v''}$ obtained and state its statistical validity and physical significance.

5. Students can obtain other representative spectra and general information about HST at the Space Telescope Science Institute operated for NASA by AURA at *http://www.stsci.edu*.

Conclusions

Cometary observations and analysis of cometary spectra are active areas of research that merge the disciplines of spectroscopy, photochemistry, and astrophysics. We believe that exposing students of advanced physical chemistry (who learn about spectroscopy and photochemistry) to astrophysics will not only introduce them to important and interesting problems but will also solidify their understanding of spectroscopy.

This analysis need not be limited to CS or cometary observations. The formulas for calculating Franck–Condon factors (eqs 8–11) can be applied to any vibronic transition as long as the molecular constants for the two electronic states are known. Therefore, one can easily apply these formulas to other interesting systems. For example, the well-known molecular iodine absorption and emission experiment (*17*) can be incorporated with the above ideas to make a more complete project. The calculations discussed above can also be extended to rotational vibronic (ro-vibronic) transitions. Then, one can link this with a discussion of selections rules, Holn–London factors, Hund's angular momentum coupling cases, etc. The possibilities are endless.

Acknowledgments

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