

LIFBASE (version 1.9)  
<http://www.sri.com/cem/lifbase>

DATABASE AND SPECTRAL SIMULATION  
for OH A-X, OD A-X,  
NO A-X, B-X, C-X, D-X  
CH A-X, B-X, C-X  
CN B-X, N<sub>2</sub><sup>+</sup> B-X,  
SiH A-X and CF A-X

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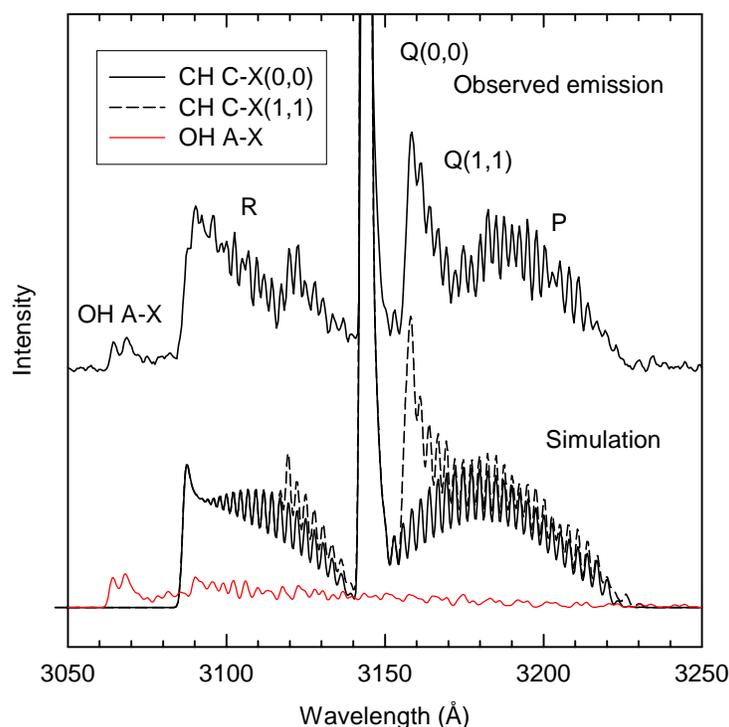
SRI report No. MP 99-009 (1999)

# LIFBASE: Database and spectral simulation program.

## 1. Goal:

This program has been designed to compile all the information available from transition probability calculations on the diatomic molecules OH, OD, CH and NO. These molecules are important in a wide variety of research fields, from basic studies in chemical dynamics to applied works in combustion. This report complements work to several manuscripts on spectroscopy of these molecules by the same authors.<sup>1-4,23,32</sup>

The output of this program furnishes Einstein emission and absorption coefficients, radiative lifetimes, transition probabilities, frequencies and Hönl-London factors for many bands of OH (A-X), OD (A-X), CH (A-X, B-X, C-X), NO (A-X, D-X), etc. Also, spectral simulation in these electronic systems can be done, including the possibility of modifying many parameters interactively.



**Figure 1. Example of optical emission spectral simulation of CH C-X in a plasma dc-reactor (Vibrational and rotational temperatures = 5500 K)**

## 2. Program description:

### 2.1. Database:

When the program initially starts, it provides a table with the quantity calculated during the last execution. The menu allows the user to change the electronic band and the spectroscopic quantities calculated.

a) The **emission coefficients** between upper levels  $v', J'$  and a lower levels  $v'', J''$  are calculated according to Schadee<sup>5</sup>, by the expression ( $s^{-1}$ ):

$$A_{v''J''}^{v'J'} = \frac{g_e'}{g_e''} \frac{64\pi^4}{3h} \frac{S_{J''}^{J'}}{2J'+1} p_{v''J''}^{v'J'} (\nu_{v''J''}^{v'J'})^3$$

the electronic degeneracy is  $g_e = (2 - \delta_{o,\Lambda})(2S+1)$ ,  $2S+1$  is the state spin multiplicity and  $\delta_{o,\Lambda} = 1$  for  $\Sigma$  states and 0 for all the others.  $S$  is the Honl-London factor,  $p$  is the transition probability and  $\nu$  is the transition frequency ( $cm^{-1}$ ).

b) The **absorption coefficients** are calculated by the expression:

$$B_{v'J'}^{v''J''} = \frac{c^2}{8\pi h (\nu_{v''J''}^{v'J'})^3} \frac{2J'+1}{2J''+1} A_{v''J''}^{v'J'}$$

The stimulated emission coefficients are

$$B_{v''J''}^{v'J'} = \frac{2J''+1}{2J'+1} B_{v'J'}^{v''J''}$$

The units ( $m^2s^{-1}J^{-1}$ ) are convenient in LIF applications and can be converted to the common ( $m^3s^{-2}J^{-1}$ ) via multiplying by the speed of light  $c$ . Oscillator strengths are also calculated and displayed.

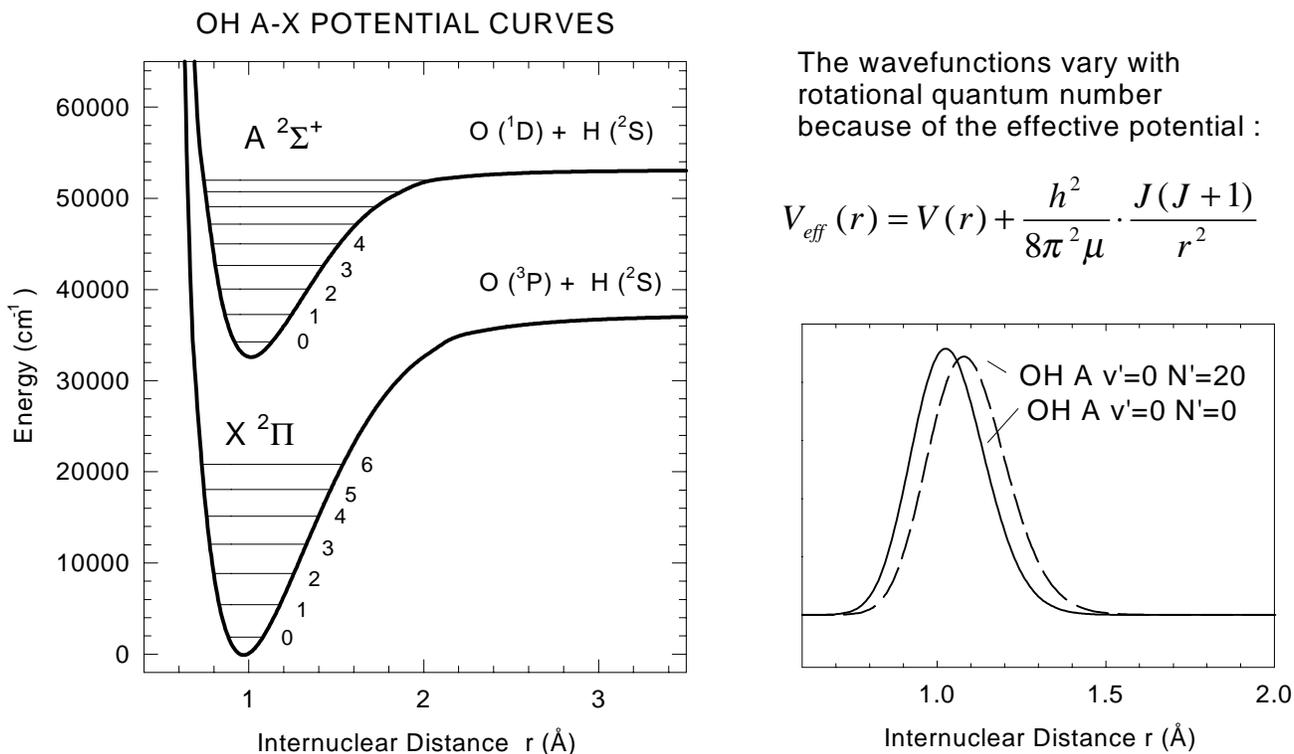
The absorption and emission coefficients have the lambda-doubling resolved for  $\Pi$  and  $\Delta$  states, and the corresponding populations must therefore be computed per lambda-doubled level as well. This is an important detail to avoid errors of factor of two when the  $\Pi \rightarrow \Sigma$  transitions are used to determine absolute number densities.

c) **Transition probabilities:** They have been previously calculated and are kept in the data base files. Transition probabilities are the integrals of the rovibrational wavefunctions of the upper and lower states together with the electronic transition moment:

$$P_{v''J''}^{v'J'} = \left( \int_{-\infty}^{\infty} \Psi_{v'J'}(r) R_e(r) \Psi_{v''J''}(r) dr \right)^2$$

The wavefunctions are computed from RKR potential curves, and  $R_e(r)$  is the electronic transition moment. See tables I -II for more detailed information on the input data for the calculations. Rotational wavefunctions are not included for the NO A-X (disk version), B-X, D-X,  $N_2^+$  B-X and CN B-X transition probabilities, those files can be obtained upon request.

The electronic transition moment can be obtained by ab initio methods, or by experimentally based techniques, like branching intensity ratios combined with either radiative lifetimes or absorption oscillator strengths. LIFBASE includes experimentally optimized transition moments or experimentally validated ab initio calculations, see references 1-3, 32 and 37.



**Figure 2. Calculation of rovibrational wavefunctions from RKR potential curves. Left: OH A and X states potential curves from RKR calculations with input data from tables I and II. Right: Effect of rotational centrifugal barrier on the wavefunctions.**

d) **Frequencies:** These are calculated from expressions derived from the corresponding Hamiltonians (most cases this is the N-formalism, known as Brown's Hamiltonian<sup>6</sup>), so the accuracy of line-positions may be limited in some cases. The units are cm<sup>-1</sup>, Å (vacuum) or Å (air).

The nomenclature of the branches is either Hund's case *a* or *b*. The program supports both cases switching with the "J" and "N" keys. In Hund's case *b* the name of the rotational branches is given by ΔN =N'-N" rather than ΔJ (N', excited state; N", ground state):

$$\text{Case a: } \Delta^N \Delta J_{FF'}(J'') \quad \text{Case b: } \Delta^J \Delta N_{FF'}(N'')$$

and ΔN or ΔJ =-2,-1,0,1,2 → O,P,Q,R,S

The rotational lines are assigned by N quantum numbers in Hund's case *b*, this notation can be changed to J numbers, Hund's case *a*. The lines with ground state terms from the spin-orbit F<sub>1</sub> : J=N+1/2 and from F<sub>2</sub> : J=N-1/2. For example:



e) Line-strengths or **Hönl-London factors:** Following the analytical expressions by Kovacs<sup>7</sup> and Earls<sup>8</sup>. The normalization is as suggested by Whiting<sup>9</sup>:

$$\sum_{J''} S_{J''}^{J'} = (2 - \delta_{0, \Lambda' + \Lambda''})(2S'+1)(2J'+1)$$

f) **Lifetimes** are calculated by:

$$\tau_{v'J'} = \frac{g_e}{\sum_{v''J''} A_{v''J''}^{v'J'}}$$

and normalized to the chosen experimental  $\tau_{v'=0}$  (in ns).

g) **Predissociation** rates ( $K_{p_{v'J'}}$ ) and **quenching** ( $K_{q_{v'J'}}$ ) rate coefficients can be included in the calculation of fluorescence quantum yields through user provided files. The program comes with the most accurate predissociation rates known, and the quenching set to zero. The column title to identify radiative lifetime is  $t_r$ , collision free lifetime is  $t_p$ , and the fluorescence quantum yield including quenching is  $Y_f$ .

Also, one can choose to study a particular vibrational band and obtain a complete table with the main and the satellite branches. Finally, the program is able to print or create a file with the selections made.

**Table I.** RKR input spectroscopic constants for the ground states of OH, OD, CH, CN and NO.

| Spectroscopic constant (cm <sup>-1</sup> )      | OH X <sup>2</sup> Π <sub>i</sub><br>(3) | OD X <sup>2</sup> Π <sub>i</sub><br>(16) | NO X <sup>2</sup> Π<br>(17) | CH X <sup>2</sup> Π<br>(18) |
|-------------------------------------------------|-----------------------------------------|------------------------------------------|-----------------------------|-----------------------------|
| Y <sub>10</sub> = ω <sub>e</sub>                | 3737.7941                               | 2721.894                                 | 1904.13455                  | 2860.7508                   |
| Y <sub>20</sub> =-ω <sub>e</sub> X <sub>e</sub> | -84.91456                               | -45.137                                  | -14.088358                  | -64.4387                    |
| Y <sub>30</sub> =ω <sub>e</sub> y <sub>e</sub>  | 0.558406                                | 0.2484                                   | 0.0100467                   | 0.3634                      |
| Y <sub>40</sub> =ω <sub>e</sub> z <sub>e</sub>  | -2.59739E-2                             | -0.0108                                  | -1.5331E-4                  | -1.537E-2                   |
| Y <sub>50</sub> =ω <sub>e</sub> a <sub>e</sub>  | -6.38868E-4                             |                                          | -9.769E-6                   |                             |
| Y <sub>60</sub> =ω <sub>e</sub> b <sub>e</sub>  | 1.34099E-5                              |                                          | -1.9142E-7                  |                             |
| Y <sub>70</sub> =ω <sub>e</sub> c <sub>e</sub>  | -4.19977E-6                             |                                          | -5.2734E-9                  |                             |
| Y <sub>01</sub> = B <sub>e</sub>                | 18.89638                                | 10.017852                                | 1.70488847                  | 14.45988                    |
| Y <sub>11</sub> =-α <sub>e</sub>                | -0.725042                               | -0.27956                                 | -0.01754158                 | -0.536541                   |
| Y <sub>21</sub> = γ <sub>e</sub>                | 8.3292E-3                               | 2.118E-3                                 | -1.4886E-5                  | 3.3315E-3                   |
| Y <sub>31</sub> = δ <sub>e</sub>                | -9.50223E-4                             | -1.1184E-4                               | 0                           | -2.158E-4                   |
| Y <sub>41</sub>                                 | 8.04060E-5                              |                                          | -4.7275E-8                  |                             |
| Y <sub>51</sub>                                 | -5.86647E-6                             |                                          | 1.0108E-9                   |                             |
| Y <sub>61</sub>                                 |                                         |                                          | 1.0108E-9                   |                             |
| Y <sub>71</sub>                                 |                                         |                                          | -6.0557E-11                 |                             |

**Table II.** RKR input spectroscopic constants for the excited states OH A, OD A, NO A,B,D and CH A,B,C. Also included are sources for radiative lifetimes(τ), predissociation rates (Kp) and electronic transition moments (R<sub>e</sub>(r)).

| Spectroscopic quantity                          | OH A <sup>2</sup> Σ <sup>+</sup><br>(3)    | OD A <sup>2</sup> Σ <sup>+</sup><br>(19) | NO A <sup>2</sup> Σ <sup>+</sup><br>(20) | NO B <sup>2</sup> Π<br>(39) | NO D <sup>2</sup> Σ <sup>+</sup><br>(39) | CH A <sup>2</sup> Δ<br>(18) | CH B <sup>2</sup> Σ <sup>-</sup><br>(21,49) | CH C <sup>2</sup> Σ <sup>+</sup><br>(21,50) |
|-------------------------------------------------|--------------------------------------------|------------------------------------------|------------------------------------------|-----------------------------|------------------------------------------|-----------------------------|---------------------------------------------|---------------------------------------------|
| T <sub>e</sub>                                  | 32683.7                                    | 32680.8                                  | 43965.7                                  |                             | 53084.7                                  | 23151.492                   | 26070                                       | 31801.5                                     |
| Y <sub>10</sub> =ω <sub>e</sub>                 | 3178.3554                                  | 2316.17                                  | 2374.372                                 | 1037.45                     | 2323.9                                   | 2914.0990                   | 2251                                        | 2840.2                                      |
| Y <sub>20</sub> =-ω <sub>e</sub> X <sub>e</sub> | -92.68141                                  | -50.433                                  | -16.159                                  | -7.472                      | -22.885                                  | -81.4002                    | -231                                        | -125.96                                     |
| Y <sub>30</sub> =ω <sub>e</sub> y <sub>e</sub>  | -1.77305                                   | -.235                                    | -3.73E-2                                 | 0.0725                      | 0.75                                     | -3.3881                     |                                             | 13.55                                       |
| Y <sub>40</sub> =ω <sub>e</sub> z <sub>e</sub>  | 0.307923                                   |                                          |                                          |                             | 0.22                                     |                             |                                             | -3.9457                                     |
| Y <sub>50</sub> =ω <sub>e</sub> a <sub>e</sub>  | -3.5494E-2                                 |                                          |                                          |                             |                                          |                             |                                             |                                             |
| Y <sub>01</sub> = B <sub>e</sub>                | 17.38922                                   | 9.1936                                   | 1.995586                                 | 1.12                        | 2.0026                                   | 14.899748                   | 13.3815                                     | 14.603                                      |
| Y <sub>11</sub> =-α <sub>e</sub>                | -0.858139                                  | -0.3181                                  | -1.8714E-2                               | -0.01348                    | 0.02175                                  | -0.63540                    | -1.4827                                     | -0.7185                                     |
| Y <sub>21</sub> = γ <sub>e</sub>                | 2.45302E-2                                 | -0.00119                                 | -4.78E-5                                 | 0.000125                    |                                          | -9.83E-3                    |                                             |                                             |
| Y <sub>31</sub> = δ <sub>e</sub>                | -1.057E-2                                  |                                          |                                          |                             |                                          | -4.042E-3                   |                                             |                                             |
| Y <sub>41</sub>                                 | 1.7445E-3                                  |                                          |                                          |                             |                                          |                             |                                             |                                             |
| Y <sub>51</sub>                                 | -1.38486E-4                                |                                          |                                          |                             |                                          |                             |                                             |                                             |
| τ <sub>v=0</sub> (ns)                           | 685±20<br>(22)                             | 680±25<br>(3)                            | 210±10<br>(23)                           | 1950±50<br>(47)             | 18.5± 1<br>(23,41)                       | 535±15<br>(24)              | 325±15<br>(24)                              | 110±15<br>(25)                              |
| R <sub>e</sub> (r)                              | (3)                                        | (3)                                      | (32)                                     | (48)                        | (42)                                     | (1)                         | (2)                                         | (33)                                        |
| Kp                                              | v'=0,1,2<br>(26)<br>v'=3 (27)<br>v'=4 (28) | v'=0-3<br>(29)                           | v'=4,5<br>(23)                           | Not<br>included             | v'=1-3<br>(23)                           | v'=1 (24)<br>v'=2 (30)      | v'=0,1<br>(34,14)                           | v'=0 (31)<br>v'=0,1 (24)                    |

**Table III.** RKR input spectroscopic constants for the ground states of OH, OD, CH, CN  $N_2^+$  and NO.

| Spectroscopic constant ( $\text{cm}^{-1}$ ) | CN $X^2\Sigma^+$<br>(35) | SiH $X^2\Pi$<br>(39,42) | CF $X^2\Pi$<br>(39) | $N_2 X^2\Sigma^+$<br>(47) |  |
|---------------------------------------------|--------------------------|-------------------------|---------------------|---------------------------|--|
| $Y_{10} = \omega_e$                         | 2068.6786                | 2041.8                  | 1308.1              | 2207.22                   |  |
| $Y_{20} = -\omega_e x_e$                    | 13.11735                 | 35.51                   | 11.1                | -16.226                   |  |
| $Y_{30} = \omega_e y_e$                     | 0.006543                 |                         | 0.093               | 4E-3                      |  |
| $Y_{40} = \omega_e z_e$                     |                          |                         | -0.0011             | -6.1E-3                   |  |
| $Y_{50} = \omega_e a_e$                     |                          |                         |                     | 3.9E-4                    |  |
| $Y_{60} = \omega_e b_e$                     |                          |                         |                     | -1.4E-5                   |  |
| $Y_{70} = \omega_e c_e$                     |                          |                         |                     | 2.0E-7                    |  |
| $Y_{01} = B_e$                              | 1.89977481               | 7.4996                  | 1.4172              | 1.93171                   |  |
| $Y_{11} = -\alpha_e$                        | -0.01737135              | -0.219                  | -0.0184             | -0.018816                 |  |
| $Y_{21} = \gamma_e$                         | -2.543E-5                |                         | 0.00011             | -6.77E-5                  |  |
| $Y_{31} = \delta_e$                         | -4.59E-7                 |                         |                     | -2.32E-6                  |  |
| $Y_{41}$                                    |                          |                         |                     |                           |  |
| $Y_{51}$                                    |                          |                         |                     |                           |  |
| $Y_{61}$                                    |                          |                         |                     |                           |  |
| $Y_{71}$                                    |                          |                         |                     |                           |  |

**Table IV.** RKR input spectroscopic constants for the excited states CN B,  $N_2^+ B$ , CF A, SiH A and NO C. Also included are sources for radiative lifetimes( $\tau$ ), predissociation rates (Kp) and electronic transition moments ( $R_e(r)$ ).

| Spectroscopic quantity   | CN B $2\Sigma^+$<br>(36) | SiH A $2\Delta$<br>(39,42) | CF A $2\Sigma^+$<br>(39) | $N_2 B^2\Sigma^+$<br>(51) | NO C $2\Pi$<br>(54,55) |  |
|--------------------------|--------------------------|----------------------------|--------------------------|---------------------------|------------------------|--|
| $T_e$                    | 25752.0                  | 24300.4                    | 42692.9                  | 25461.11                  | 51572.9                |  |
| $Y_{10} = \omega_e$      | 2161.458                 | 1858.9                     | 1780.45                  | 2421.14                   | 2381.3                 |  |
| $Y_{20} = -\omega_e x_e$ | -18.219                  | -99.175                    | -30.73                   | -24.07                    | -15.702                |  |
| $Y_{30} = \omega_e y_e$  | -0.486                   |                            |                          | -0.3                      |                        |  |
| $Y_{40} = \omega_e z_e$  | 0.04                     |                            |                          | -0.0667                   |                        |  |
| $Y_{50} = \omega_e a_e$  | 0.00693                  |                            |                          |                           |                        |  |
| $Y_{01} = B_e$           | 1.96891                  | 7.4664                     | 1.7228                   | 2.0857                    | 2.0155                 |  |
| $Y_{11} = -\alpha_e$     | -0.020337                | -0.3445                    | -0.0189                  | -0.0212                   | -0.03244               |  |
| $Y_{21} = \gamma_e$      | -5.9E-5                  | -0.0418                    | -0.0028                  | -5E-4                     |                        |  |
| $Y_{31} = \delta_e$      | -7.71E-5                 |                            |                          | -8.8E-5                   |                        |  |
| $Y_{41}$                 | 3.1E-6                   |                            |                          |                           |                        |  |
| $Y_{51}$                 |                          |                            |                          |                           |                        |  |
| $\tau_{v=0}$ (ns)        | $65 \pm 2$ (38)          | $520 \pm 15$ (43)          | $26.5 \pm 2$ (45)        | $67 \pm 1$ (52)           | $28 \pm 1$ (41)        |  |
| $R_e(r)$                 | (37)                     | (44)                       | (46)                     | (53)                      | (42)                   |  |
| Kp                       | Not included             | (43)                       | $v=2$ (46)               |                           | $v'=0,1$ (41)          |  |

## 2.2. Spectral simulation:

Before the spectra are calculated, there are a number of options:

### 2.2.1. Intensities:

LIFBASE permits the calculation of several kinds of spectra:

a) **Emission:** The intensity is given by:

$$I_{v''J''}^{v'J'} \propto N_{v'J'} \cdot \frac{A_{v''J''}^{v'J'}}{\sum_{v''J''} A_{v''J''}^{v'J'} + Kq_{v'J'} \cdot P + Kp_{v'J''}} \cdot (1 - e^{-\frac{t}{\tau}})$$

P is the pressure, and  $\tau$  is the effective lifetime:

$$\tau = \frac{1}{\sum_{v''J''} A_{v''J''}^{v'J'} + Kq_{v'J'} \cdot P + Kp_{v'J''}}$$

b) **Absorption:**

$$\ln \frac{I}{I_0} \propto N_{v''J''} \cdot B_{v'J'}^{v''J''} \cdot \nu_{v''J''}^{v'J'}$$

c) **Excitation LIF:** Laser-induced fluorescence is a two-step process: first, there is absorption, and second, emission from the populated level:

$$I_{v''J''} \propto N_{v''J''} \cdot B_{v'J'}^{v''J''} \cdot \sum_{v''J''} A_{v''J''}^{v'J'} \cdot \tau \cdot (1 - e^{-\frac{t}{\tau}})$$

This expression is valid for LIF when:

- The intensity of the laser field is low and there are no saturation effects (i.e. stimulated emission is negligible).
- The detection system is collecting the total fluorescence, with the same detection efficiency for all the wavelengths.
- Polarization effects are negligible.
- Vibrational or rotational relaxation effects are not important, because the fluorescence is assumed to come from the laser-populated level in the excited state.

- The pumping laser is shorter than the effective lifetime (otherwise is better to integrate in time the whole fluorescence signal)

d) **DFWM**: This option can be used for isolated branches only because polarization and geometrical factors are not included:

$$I_{v''J''} \propto N_{v''J''}^2 \cdot (B_{v''J''})^4$$

### 2.2.2. Lineshapes and linewidths:

The intensities are convoluted with lineshapes chosen among triangular, gaussian and lorentzian types. For example, the Lorentzian profile is taken into account by:

$$L(v - v_0) = \frac{\Delta v}{(v - v_0)^2 + (\Delta v / 2)^2}$$

The initial bandwidth ( $\Delta v = \text{FWHM}$ ) of these shapes is the input parameter "Resolution", in Å, which corresponds to the expected value by instrumental (laser bandwidth, monochromator). Physical broadening (Doppler, collisional broadening, natural linewidth, etc) is convoluted with the instrumental lineshape.

The broadening mechanisms supported in the current version are:

- **Natural linewidth** and **predissociation**. The bandwidth for any lineshape is given by:

$$\Delta v_{\tau} = \frac{1}{2\pi c \tau} \text{ in cm}^{-1}, \text{ and } \Delta \lambda = 10^{-8} \cdot \Delta v \cdot \lambda^2 \text{ in Å}$$

The lifetime  $\tau$  is computed as in section 2.2.1. The optimal lineshape for this broadening is Lorentzian.

- The **Doppler broadening** is given by the general expression:

$$\Delta v_D = 7.16 \cdot 10^{-7} \cdot v \cdot \sqrt{\frac{T}{M}} \text{ in cm}^{-1}$$

T is the gas temperature and it is independent of the vibrational and rotational population distributions, M is the mass of the molecule. The resulting lineshape broadening is best represented by a Gaussian.

- The **collisional broadening** is given by:

$$\Delta\nu_c = a \cdot \left( \frac{P}{760} \right) \left( \frac{300}{T} \right)^b$$

a is in  $\text{cm}^{-1}$ , P and T are the pressure and translational temperature of the system.

- The **instrumental linewidth** ( $\Delta\nu_i$ ), it can be either the laser bandwidth or the monochromator resolution. Gaussian, Lorentzian and Voigt lineshapes are valid.

The line broadening contributions are convoluted with appropriated Lorentzian, Gaussian or Voigt lineshapes. For example, Gaussian and Lorentzian lineshapes give a Voigt lineshape.

The program displays the FWHM value given by Doppler, collisional and instrumental convoluted broadening, but each line can have a different linewidth if the predissociation dominates the broadening.

### 2.2.3. Frequency/Wavelength shifts:

- Doppler shift:

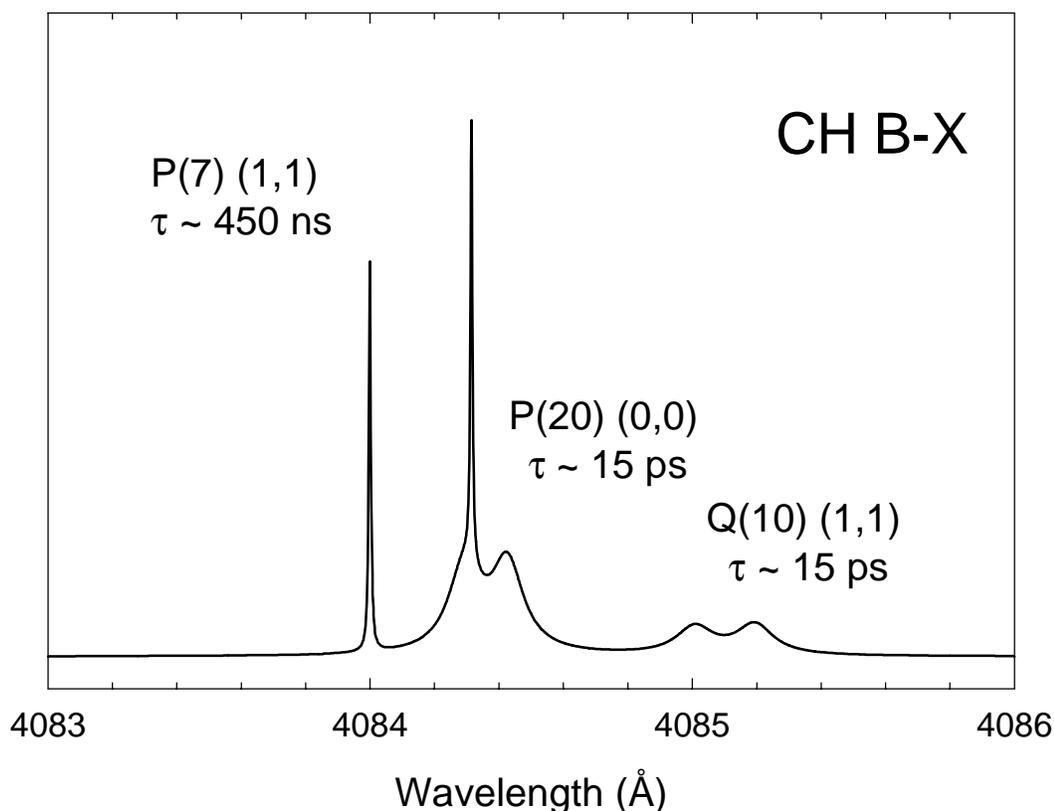
$$\Delta\nu_d = -\nu \cdot \left( \frac{v_m}{c} \right)$$

$\nu$  is the frequency of the transition, c is the speed of light and  $v_m$  is the velocity of the gas in the detector direction.

- Collisional shift: Calculated with a similar expression to collisional broadening

$$\Delta\nu_c = -d \cdot \left( \frac{P}{760} \right) \left( \frac{300}{T} \right)^e$$

d is in  $\text{cm}^{-1}$ , P and T are the pressure and translational temperature of the system.



**Figure 3. Example of predissociation broadening in the CH B-X system calculated with LIFBASE Absorption spectra.  $T_{\text{vib}}=1500$  K,  $T_{\text{rot}}=2500$  K. Instrumental resolution  $0.007$  Å**

#### 2.2.4. Initial populations:

The program is able to handle Boltzmann and non-Boltzmann distributions. In the initial simulation is assumed thermalized: main temperature (translational) is equal to the vibrational and rotational temperature in all levels. If a vibrational population is zero, the corresponding vibrational level will be skipped in the calculation. The thermal rotational ( $T_{\text{rot}}$ ) and vibrational ( $T_{\text{vib}}$ ) populations are calculated following the Boltzmann's distributions:

$$N_{v,J} = N_o \cdot f_B(v,J) = N_o \cdot \frac{e^{-\frac{E_v(v)}{kT_{\text{vib}}}} \cdot (2J+1) \cdot e^{-\frac{E(J)}{kT_{\text{rot}}}}}{Q_{\text{vib}} \cdot Q_{\text{rot}} \cdot Q_{\text{elec}}}$$

$N_o$  is the total number density, and  $f_B(v,J)$  is the Boltzmann fraction;  $Q_{\text{vib}}$  and  $Q_{\text{rot}}$  are the rotational and vibrational partitions calculated numerically, and  $Q_{\text{elec}}$  is the electronic partition function ( $Q_{\text{elec}} = g_e$ ).

The temperature in the main menu is the translational temperature and is used for the calculation of Doppler and collisional broadening and collisional shifts even if the rotational and vibrational distributions are non-thermal. To see or modify vibrational and rotational state populations

### 2.2.5. Other parameters:

a) **Wavelength range** (in Å). This is the interval to study.

b) **Units:** Å (vacuum or air) or  $\text{cm}^{-1}$ . The conversion from vacuum wavelengths to air values (15 C, 760 Torr), taking into account the air refraction index (n), it is given by the Edlen formula:

$$\Delta\lambda = \lambda_{\text{air}}(n - 1) = \lambda_{\text{air}} \left( 8342.13 + \frac{2406030}{130 - \sigma^2} + \frac{15997}{38.9 - \sigma^2} \right) \cdot 10^{-8}$$

where  $\sigma = 1/\lambda$  ( $\sigma$  in  $\mu\text{m}^{-1}$ ), and  $\lambda_{\text{air}} = \lambda_{\text{vacuum}} - \Delta\lambda$

c) **Experimental file:** An experimental file can be included for comparison to calculations. It must be in angstroms, nm or  $\text{cm}^{-1}$

The database handles the additional factors needed for the spectral calculation, including lineshape convolution, lifetimes, predissociation and collisional constants. Spectra can be simulated including many vibrational levels for a wide range of wavelength. The main limitation in the simulation is given by the computer memory. To reach high resolution it is better to use a few vibrational bands and a narrow wavelength range.

### 2.2.6. Optimization of the spectral simulation:

After the calculation of the initial spectra, a full menu for optimization of this simulation is presented:

a) Vibrational populations can be changed easily. Rotational populations have a special and sophisticated menu to help in the optimization. When a **non-Boltzmann** distribution is chosen, populations can be modified by spin-orbit distributions, lambda-doubling distribution, and individual rotational levels.

b) The spectra are represented in overlapped or split windows. Contributions of different vibrational bands can be visualized with area or contour plots. Residuals are also amongst the choices.

c) Experimental settings: resolution, level of noise, lineshape and pressure (if quenching rates are involved), and gated detection can be varied in an interactive way.

d) There are tools to help comparisons: The experimental spectra can be wavelength and baseline corrected, and can be changed by another file. The screen can be enlarged by vertical and horizontal zooms. A model subtraction is feasible, the program interpolates the model and removes unwanted contributions to the experimental spectra (especially useful in emission studies complicated with energy transfer). Assignment of the rotational transitions is another tool available and simplifies the analysis of the spectra.

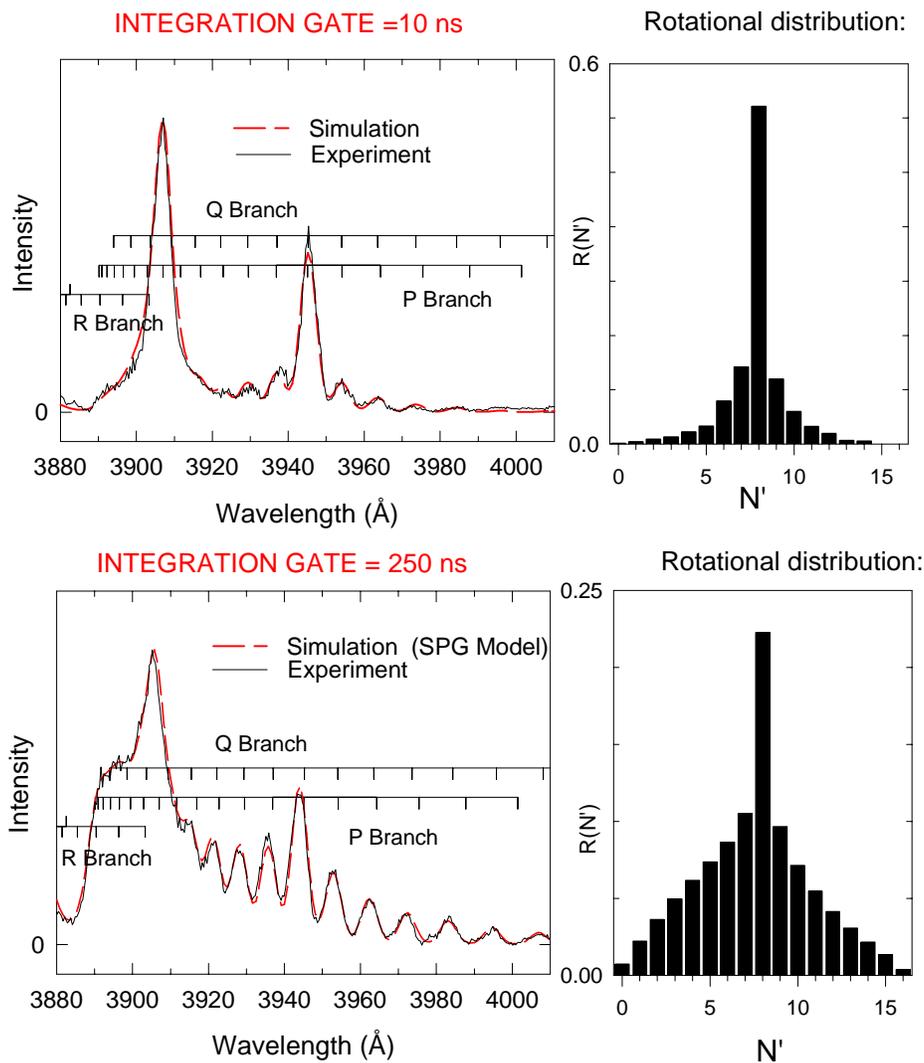
e) Finally, the file menu allows load and save simulations, experimental spectra and rotational distributions.

### 3. Examples

The database provides absolute values of the spectroscopic coefficients, and they can be used to obtain **absolute number densities**. Flames and plasmas are chemical systems where the determination of radical concentrations are vital tests of kinetic models of the chemistry. Examples of absolute determination of ground state number densities on those systems, using laser-induced fluorescence and LIFBASE values, are given in references 10-12.

The variation of the absorption and emission coefficients with vibration and rotational quantum numbers is important for obtaining accurate **rotational and vibrational temperatures**<sup>13</sup>. LIFBASE include the electronic transition moment, rovibrational wavefunctions and rotational Hönl-London factors in the spectroscopic computations. This approach is superior to the use of just Hönl-London factors, which has been the common situation in many studies.

The simulation routine lets one estimate **complex population distributions**, resulting from energy transfer, photodissociation, and/or laser excitation. Examples of vibrational and rotational energy transfer evaluated with LIFBASE can be found in references 1,2,4, 13,14 and 15.



**Figure 4. Example of non-thermal population distribution analysis. Fluorescence scan after pumping R(7) CH B-X (0,0) in a methane/oxygen flame at 8 Torr. Up: Integrating the first 10 ns of fluorescence. Down: Time-integration of the total fluorescence. Both spectra are along the retrieved CH B  $v'=0$  rotational distributions.**

## 4. Software Details:

### 4.1. Installation:

The program is distributed by internet download and CD-ROM format. To install the software click in the setup.exe icon and follow the instructions.

### 4.2. Program files:

LIFBASE.EXE: main program.

LIFBASE.PDF: Adobe acrobat version of the manual. Download free Acrobat reader at [www.adobe.com](http://www.adobe.com).

LIFBASE.SYS: File with programmable settings and some general molecular parameters.

### 4.3. Data files:

Each molecule has its own subdirectory. For example, in OH:

- OHA. SPC and OHX. SPC, spectroscopic data for the excited and ground states. The two first parameters give information about the spectroscopic constants and kind of Hamiltonian (it is Brown's usually).

- OHAV0.DAT, OHAV1.DAT, etc.: Data on experimental lifetimes, predissociation and quenching rates. The program calculates radiative lifetimes, but if it finds data different from zero in this column, then it will take the data as the radiative lifetimes. The program is able to recognize predissociative rates ( $s^{-1}$ ) or free collision lifetimes (ns) automatically. Quenching rates are in laboratory units  $\mu s^{-1} Torr^{-1}$

Each transition has its own subdirectory. For example, in OH\AX:

- OHAX00,etc...: Transition probabilities of OH (A-X) (0,0),etc...

### 4.4. Output and input files structure:

- Output model files: wavelength, as many columns as vibrational levels, total model.

- Output rotational distribution files: (\*.rot)  
Rotational number J, N(F1), N(F2).

In the case of lambda doubling:

Rotational number J, N(F1e),N(F2f),N(F1f),N(F2e).

- Output vibrational distribution files: (\*.vib)

Vibrational number v, normalized vibrational population.

- Input spectra file: Wavelength (Å), Intensity. File columns can be separated by blanks, tabs or commas.

- Input rotational and vibrational distributions input files follow the structure of the output files. It is simple to create files from other applications that can be imported to LIFBASE.

#### **4.5. Hardware and Software requirements:**

a) Operative System : Windows 95/98/Me and Windows NT/2000/XP.

b) Hardware: Pentium microprocessor, 5 Mb of hard drive space, screen resolution 800 x 600 pixels or better.

If you have any problem or suggestions, please contact  
Jorge Luque.  
Phone: (650)-859-3895  
Fax: (650)-859-6196  
e-mail: LUQUE@SRI.COM

#### **5. How to reference LIFBASE:**

At this point in time, the best way to reference LIFBASE is:

J. Luque and D.R. Crosley, "LIFBASE: Database and Spectral Simulation Program (Version 1.5)", SRI International Report MP 99-009 (1999).

The use of specific emission and absorption coefficients will be better acknowledged referencing the appropriate Journal of Chemical Physics papers<sup>1-3,32</sup>.

#### **6. Acknowledgments:**

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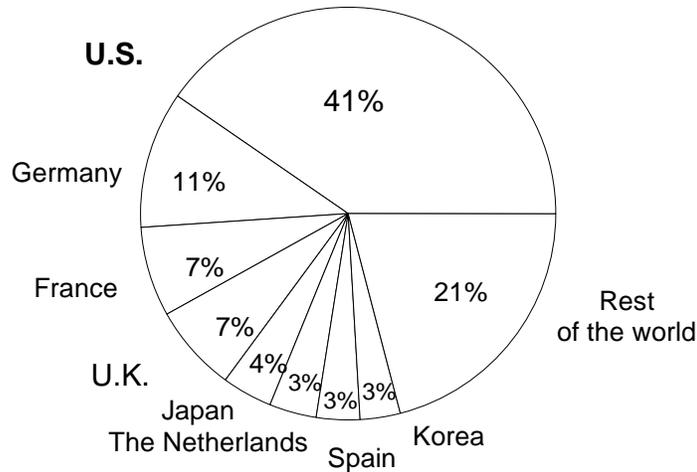
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Until the present date, the program has been requested by more than one thousand researchers in universities, national labs and corporations worldwide. About 40% of the users are in the United States. The program is being requested by a noticeable number of not only universities, but also National Labs, Defense related laboratories and private corporations.

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