NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

## Technical Report 32-1166

# Approximate Formulas for the Intensity of Electronic Transitions in Diatomic Molecules

*T. M. Helliwell*
***Harvey Mudd College***
*W. A. Menard*
***Jet Propulsion Laboratory***

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

September 1, 1967

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

## *Technical Report 32-1166*

# *Approximate Formulas for the Intensity of Electronic Transitions in Diatomic Molecules*

*T. M. Helliwell*
*Harvey Mudd College*
*W. A. Menard*
*Jet Propulsion Laboratory*

Approved by:

Laumann

E. A. Laumann, *Manager*
Aerodynamic Facilities Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

September 1, 1967

**TECHNICAL REPORT 32-1166**

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

# Acknowledgment

The authors wish to thank T. Horton, J. Spiegel, G. Thomas, and F. Wolf for very helpful discussions.

# Contents

## Tables

## Figures

# Abstract

Approximate formulas are derived for the intensity of diatomic molecular electronic transitions. The formulas correspond to various models of the spectrum, ranging from a monochromatic approximation to others in which more details of the vibrational and rotational structure are taken into account. Some of these methods are well known, while others appear to be new. Choice of the appropriate method in a given circumstance depends upon the spectral shape, knowledge of the molecular parameters, and the desired accuracy of the calculation. Each model is applied to the CN violet system to illustrate its accuracy.

# Approximate Formulas for the Intensity of Electronic Transitions in Diatomic Molecules

## I. Introduction

A molecular spectrum arising from electronic transitions consists of many lines that correspond to different initial and final vibrational and rotational states. Lines are also broadened and shifted by various mechanisms making details of the spectrum difficult to predict. However, for some purposes, the interest is primarily in the total radiation or in a rough idea of local features. In such cases, calculations can be considerably simplified. We will derive several approximate formulas connected with different models of the spectrum which are useful in problems of this kind.

We begin by defining notation and reviewing some basic relationships. The energy levels of a molecule will be denoted as shown in Fig. 1. A given electronic state is composed of many vibrational states (with energy $E_v$ above the lowest vibrational level) and rotational states (with energy $E_J$ above the lowest rotational level in a given vibrational state). As shown in Fig. 1, the lowest level in the electron state has energy $E_e$ above the ground state of the molecule.

If the molecules are in thermal equilibrium and obey Boltzmann statistics, the fraction of all molecules in a particular $evJ$ level is

$$\frac{N_{evJ}}{N} = \frac{g_e\,(2J+1)\exp\left[-\dfrac{(E_e+E_v+E_J)}{kT}\right]}{Q} \tag{1}$$

where $g_e$ is the electron degeneracy given by $g_e = 2S + 1$ for $\Sigma$ states and $2\,(2S + 1)$ for all other states. Here, $S$ is the spin quantum number of the electron state. The denominator

$$Q = \sum_{all\ e,v,J} g_e\,(2J+1)\exp\left[-\frac{(E_e+E_v+E_J)}{kT}\right] \tag{2}$$

is the total partition function.

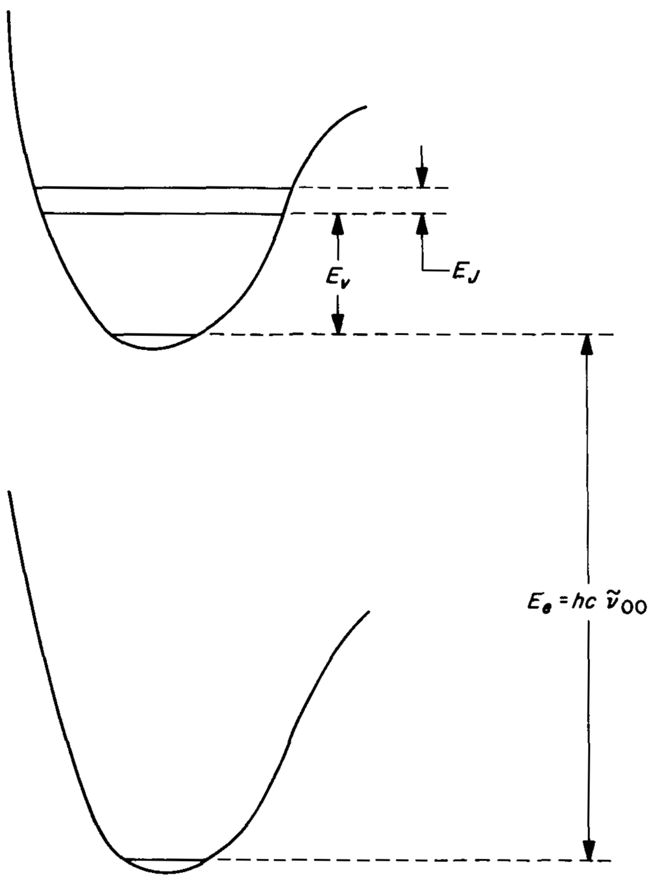


Fig. 1. Energy level diagram

The fraction of molecules in a given electron state, regardless of the vibrational or rotational level, is

$$F_{e,T} \equiv \frac{N_e}{N} = \frac{\sum\limits_{v,J} N_{evJ}}{N} = \frac{g_e \exp\left(-\frac{E_e}{kT}\right) \sum\limits_v \exp\left(-\frac{E_v}{kT}\right) \sum\limits_J (2J+1) \exp\left(-\frac{E_J}{kT}\right)}{Q} \tag{3}$$

Equation (1) can then be rewritten as

$$\frac{N_{evJ}}{N} = F_{e,T} \frac{\exp\left(-\frac{E_v}{kT}\right)(2J+1)\exp\left(-\frac{E_J}{kT}\right)}{\sum\limits_v \exp\left(-\frac{E_v}{kT}\right) \sum\limits_J (2J+1)\exp\left(-\frac{E_J}{kT}\right)} \tag{4}$$

We now write the rotational energies as

$$E_J = J(J+1)\,hcB_e \tag{5}$$

where $B_e$ is a constant depending only on the electron state, and not on the vibrational state. This approximation is accurate enough for our purposes (Ref. 1). The rotational state with the highest population corresponds to

$$\frac{d}{dJ}(2J+1)\exp\left[-\frac{J(J+1)\,hcB_e}{kT}\right] = 0$$

or

$$J_{max} = \left(\frac{kT}{2hcB_e}\right)^{1/2} - \frac{1}{2}$$

Supposing the gas to be hot enough that $J_{max} >> 1$, the rotational partition function

$$Q_J \equiv \sum_J (2J+1)\exp\left(-\frac{E_J}{kT}\right) \tag{6}$$

can be approximated by an integral

$$Q_J \cong \int_0^\infty (2J+1)\exp\left[-\frac{J(J+1)\,hcB_e}{kT}\right] dJ = \frac{kT}{hcB_e} \tag{7}$$

Since we have assumed the rotational constant to be independent of the vibrational level, the total partition function can be factored, and Eq. (4) can be written as

$$\frac{N_{evJ}}{N} = F_{e,T} \frac{\exp\left(-\frac{E_v}{kT}\right)}{Q_v} \frac{(2J+1)\exp\left(-\frac{E_J}{kT}\right)}{Q_J} \tag{8}$$

where the vibrational partition function is

$$Q_v = \sum_v \exp\left(-\frac{E_v}{kT}\right) \tag{9}$$

Suppose a molecule makes a transition from an upper state $n$ to a lower state $m$. If $A_{nm}$ is the Einstein transition probability, $hc\tilde{\nu}_{nm}$ the transition energy (with the wave number $\tilde{\nu}_{nm}$ in cm$^{-1}$), and the number density of molecules in the upper state $N_n$, the total emitted intensity is

$$I^{nm} = N_n hc\tilde{\nu}_{nm} A_{nm} \tag{10}$$

The transition probability is related to the emission oscillator strength $f_{em}^{nm}$ by

$$A_{nm} = \frac{8\pi^2 e^2 \tilde{\nu}_{nm}^2}{mc} f_{em}^{nm} \tag{11}$$

thus, defining $r_0 \equiv e^2/mc^2 =$ *classical electron radius*,

$$I^{nm} = N_n \cdot 4\pi \cdot 2hc^2 \pi r_0 \tilde{\nu}_{nm}^3 f_{em}^{nm} \tag{12}$$

The intensity per steradian is obtained by dividing by $4\pi$. If all quantities are expressed in cgs units, the right-hand side must be multiplied by $10^{-7}$ to convert to the common units of W/cm$^3$. Numerically, the total radiated intensity of the $n \rightarrow m$ transition per cubic centimeter of gas can then be written

$$I^{nm} = 1.32 \times 10^{-23} \tilde{\nu}_{nm}^3 N_n f_{em}^{nm} \text{ W/cm}^3 \tag{13}$$

It should be emphasized that in these formulas, and in those that follow, a negligible self-absorption is assumed so that only optically thin layers of radiating gas are considered.

The oscillator strength $f_{em}^{nm}$ can be written approximately (Ref. 1) as the product of an oscillator strength $f_{em}^{elec}$ for the electron transition as a whole, and a Franck-Condon factor $q_{v'v''}$ between given vibrational levels. Therefore,

$$f_{em}^{nm} = f_{em}^{elec} q_{v'v''} \tag{14}$$

is related to the intensity of transitions from a completely specified upper state $(e', v', J')$ to lower states having definite electron and vibrational levels ($e''$ and $v''$), but *all* allowed rotational levels $J''$. Franck-Condon factors obey the sum rule

$$\sum_{v''} q_{v'v''} = 1$$

thus, if one sums over all final vibrational levels,

$$\sum_{v''} f_{em}^{nm} = f_{em}^{elec} \sum_{v''} q_{v'v''} = f_{em}^{elec} \tag{15}$$

which shows the physical meaning of $f_{em}^{elec}$. The approximate separation of the oscillator strength into electronic and vibrational parts is a conventional procedure, but is not always very accurate. The oscillator strength will be separated in the following formulas, but the two parts can be easily recombined if desired.

Using Eqs. (12), (8), and (14), the following is obtained:

$$\frac{I^{e'v'J' \rightarrow e''v'' \, all \, J''}}{N} = 4\pi \cdot 2hc^2 \pi r_0 \tilde{\nu}_{J' \rightarrow J''}^3 f_{em}^{elec} q_{v'v''}$$
$$\times F'_{e,T} \frac{\exp\left(-\frac{E'_v}{kT}\right)}{Q'_v} \frac{(2J'+1)\exp\left(-\frac{E'_J}{kT}\right)}{Q'_J} \tag{16}$$

According to the selection rule $\Delta J = 0, \pm 1$, three (or sometimes two) lines are involved. Therefore, $\tilde{\nu}_{J' \rightarrow J''}^3$ must be an average for these lines arising from a given $J'$ level. They are actually so close together that for our purposes no important ambiguity is raised.

It is sometimes convenient to rewrite Eq. (16) in terms of properties of the *lower* electron state. From Eqs. (3), (6), and (9) we have

$$F'_{e,T} = \frac{g'_e Q'_v Q'_J \exp\left(-\frac{E'_e}{kT}\right)}{Q}$$

and

$$F''_{e,T} = \frac{g''_e Q''_v Q''_J \exp\left(-\frac{E''_e}{kT}\right)}{Q} \tag{17}$$

Also, emission and absorption oscillator strengths are related by

$$g'_e f_{em}^{elec} = g''_e f_{abs}^{elec} \tag{18}$$

so one obtains (Fig. 2)

$$f_{em}^{elec} F'_{e,T} = \frac{Q'_v Q'_J}{Q''_v Q''_J} \exp\left[-\frac{E'_e - E''_e}{kT}\right] f_{abs}^{elec} F''_{e,T} \tag{19}$$

Note also from Fig. 2 that

$$hc\tilde{\nu}_{J' \rightarrow J''} = E'_e + E'_v + E'_J - (E''_e + E''_v + E''_J)$$

or

$$E'_e - E''_e + E'_v + E'_J = hc\tilde{\nu}_{J' \rightarrow J''} + E''_v + E''_J \tag{20}$$

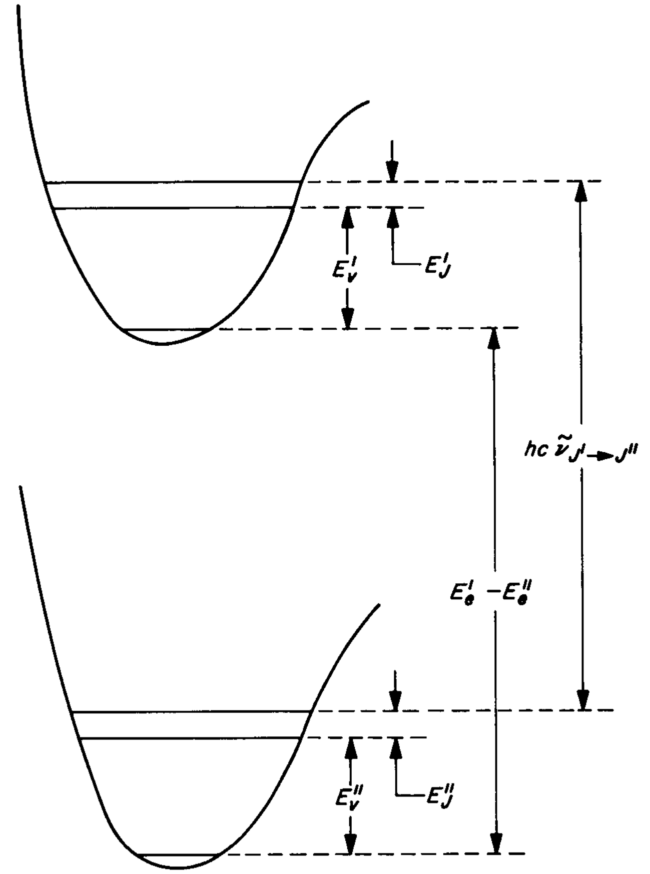


Fig. 2. Upper and lower states

Therefore, Eq. (16) can be rewritten as

$$\frac{I^{e'v'J' \to e''v''\,all\,J''}}{N} =$$

$$4\pi \cdot 2hc^2\pi r_0 \tilde{\nu}^3_{J' \to J''} f^{elec}_{abs} F''_{e,T} \exp\left(-\frac{hc\tilde{\nu}_{J' \to J''}}{kT}\right)$$

$$\times\, q_{v'v''} \frac{\exp\left(-\frac{E''_v}{kT}\right)}{Q''_v} \frac{(2J' + 1)\left(\exp - \frac{E''_J}{kT}\right)}{Q''_J} \tag{21}$$

## II. The Smoothed Rotational Model

The first model we will discuss is the smoothed rotational model, in which individual lines are smeared out to obtain a continuous spectrum. That is, the set of lines belonging to a given vibrational transition will be spread out over a continuum of frequencies, while retaining the original total intensity in any frequency interval containing many lines. For given $v'$ and $v''$, we define $\tilde{\nu}_0^{v'v''}$ by $hc\tilde{\nu}_0^{v'v''} = E'_e + E'_v - E''_e - E''_v$. Since rotational states have energy $J(J+1)\,hcB_e$ above the $J = 0$ state, it follows that the wave number difference between the $J' \to J''$ line and $\tilde{\nu}_0^{v'v''}$ is

$$\tilde{\nu} - \tilde{\nu}_0^{v'v''} = J'(J'+1)B'_e - J''(J''+1)B''_e \tag{22}$$

Since $J$ can change by at most one unit in the transition, and since we have previously assumed that large $J$-values predominate, we approximate $J' \cong J'' \equiv J$, so that

$$\tilde{\nu} - \tilde{\nu}_0^{v'v''} \cong J(J+1)(B'_e - B''_e) \tag{23}$$

Smoothing out the rotational structure means that we treat $J$ as a continuous variable. Differentiation of Eq. (23) gives $d\tilde{\nu} = (2J+1)\,(B'_e - B''_e)\,dJ$. We then spread the $J^{th}$ line over the interval $dJ = 1$ (i.e., just smoothing it out to meet the neighboring line $J + 1$), so that the range of wave numbers covered by the line is

$$\Delta\tilde{\nu} = (2J+1)\,|B'_e - B''_e| \tag{24}$$

using absolute value signs to make $\Delta\tilde{\nu}$ positive, by convention.

Now, let $I_{\tilde{\nu}}\Delta\tilde{\nu}$ be the intensity in the wave number interval $\Delta\tilde{\nu}$. From Eqs. (23) and (24), we have

$$(2J+1)\exp\left(-\frac{E''_J}{kT}\right) =$$

$$(2J+1)\exp\left(-\frac{J(J+1)\,hcB''_e}{kT}\right) =$$

$$\frac{\Delta\tilde{\nu}}{|B'_e - B''_e|}\exp\left[-(\tilde{\nu} - \tilde{\nu}_0^{v'v''})\frac{hc}{kT}\frac{B''_e}{(B'_e - B''_e)}\right] \tag{25}$$

so that Eq. (21) becomes

$$I_{\tilde{\nu}}\Delta\tilde{\nu} =$$

$$4\pi \cdot 2hc^2\pi r_0\tilde{\nu}^3 \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) N F''_{e,T} \frac{f^{elec}_{abs}}{Q''_v} \frac{hcB''_e}{kT\,|B'_e - B''_e|}$$

$$\times\, q_{v'v''} \exp\left[-\frac{E''_v + \frac{hcB''_e}{B'_e - B''_e}(\tilde{\nu} - \tilde{\nu}_0^{v'v''})}{kT}\right]\Delta\tilde{\nu} \tag{26}$$

At a given wave number, several vibrational transitions may contribute, so one must sum over $v'$ and $v''$:

$$I_{\tilde{\nu}}^{total}\,\Delta\tilde{\nu} =$$

$$4\pi \cdot 2hc^2\pi r_0 \tilde{\nu}^3 \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) N F''_{e,T} \frac{f_{abs}^{elec}}{Q''_v} \frac{hcB''_e}{kT\,|B'_e - B''_e|}$$

$$\times \sum_{v'v''} q_{v'v''} \exp\left[-\frac{E''_v + \dfrac{hcB''_e}{B'_e - B''_e}(\tilde{\nu} - \tilde{\nu}_0^{v'v''})}{kT}\right]\Delta\tilde{\nu} \tag{27}$$

Summing over those values of $v'$ and $v''$ for which

$\tilde{\nu}_0^{v'v''} \leqq \tilde{\nu}$ (if $B'_e > B''_e$)

$\tilde{\nu}_0^{v'v''} \geqq \tilde{\nu}$ (if $B'_e < B''_e$)

It is also common to treat the intensity as a function of wavelength. Using $I_\lambda \Delta\lambda = I_{\tilde{\nu}}\Delta\tilde{\nu}$, $\tilde{\nu} = 1/\lambda$, and $\Delta\tilde{\nu} = \Delta\lambda/\lambda^2$, it follows that

$$I_\lambda^{total}\,\Delta\lambda =$$

$$4\pi \cdot 2hc^2\pi r_0 \frac{1}{\lambda^5} \exp\left(-\frac{hc}{\lambda kT}\right) N F''_{e,T} \frac{f_{abs}^{elec}}{Q''_v} \frac{hcB''_e}{kT\,|B'_e - B''_e|}$$

$$\times \sum_{v'v''} q_{v'v''} \exp\left[-\frac{E''_v + \dfrac{hcB''_e}{B'_e - B''_e}\left(\dfrac{1}{\lambda} - \dfrac{1}{\lambda_0^{v'v''}}\right)}{kT}\right]\Delta\lambda \tag{28}$$

summed over $v'$ and $v''$ for which

$\lambda_0^{v'v''} \geqq \lambda$ (if $B'_e > B''_e$)

$\lambda_0^{v'v''} \leqq \lambda$ (if $B'_e < B''_e$)

These formulas for the smoothed rotational model have been derived before in Refs. (2–4). There are differences in notation between the various results, and some actual differences that are not important in the temperature and wavelength range assumed here ($\tilde{\nu}/T \gtrsim 2$).

We have programmed Eq. (28), and part of the computed spectrum of the CN violet transition ($B^2\Sigma \rightarrow X^2\Sigma$) is reproduced (see Fig. 4). A numerical integration over the spectrum can then be performed. The total radiated intensity per molecule (at 7000°K) for this transition is shown in Table 1.

## III. The First Vibrational Model

The smoothed rotational model just presented is highly accurate for calculating total radiation or the averaged local details of the spectrum. However, considerable labor is required to apply this method to particular cases—perhaps more than is justified by knowledge of the physical parameters or the desired accuracy of the result. Fortunately, it is possible to derive simpler formulas that correspond to less detailed spectral models.

To obtain the total radiated intensity per molecule in going from electron state $e'$ to electron state $e''$ (i.e., including all bands), one can sum Eq. (16) over $v'$, $v''$, and $J''$. The result is

$$\frac{I^{e'\rightarrow e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 \frac{f_{em}^{elec} F'_{e,T}}{Q'_v Q'_J} \sum_{v'} \sum_{v''} q_{v'v''} \exp\left(-\frac{E'_v}{kT}\right)$$

$$\times \sum_{J'} (2J' + 1) \exp\left(-\frac{E'_J}{kT}\right) \tilde{\nu}^3_{J'\rightarrow J''} \tag{29}$$

Expressing in terms of densities in the lower electron state (Eq. (19) along with the definition $E'_e - E''_e \equiv hc\tilde{\nu}_{00}$ from Fig. 1) can be used to obtain an alternate formula

$$\frac{I^{e'\rightarrow e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 \frac{f_{abs}^{elec} F''_{e,T}}{Q''_v Q''_J} \exp\left(-\frac{hc\tilde{\nu}_{00}}{kT}\right)$$

$$\times \sum_{v'} \sum_{v''} q_{v'v''} \exp\left(-\frac{E'_v}{kT}\right)$$

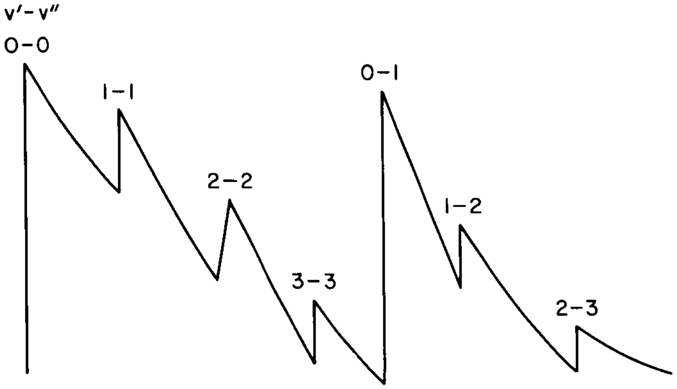
$$\times \sum_{J'} (2J' + 1) \exp\left(-\frac{E'_J}{kT}\right) \tilde{\nu}^3_{J'\rightarrow J''} \tag{30}$$

As a simplification, we now neglect all rotational structure, and assume, that to a good approximation for given vibrational states, all light is emitted at a single average frequency. That is, let

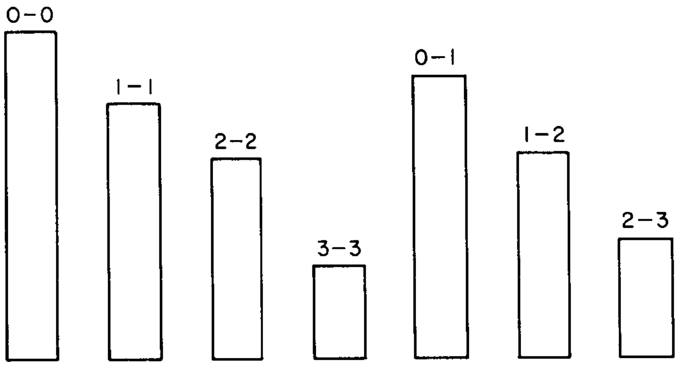
$$\sum_{J'} (2J' + 1) \exp\left(-\frac{E'_J}{kT}\right) \tilde{\nu}^3_{J'\rightarrow J''} =$$

$$\tilde{\nu}^3_{v'v''} \sum_{J'} (2J' + 1) \exp\left(-\frac{E'_J}{kT}\right) \equiv \tilde{\nu}^3_{v'v''} Q'_J \tag{31}$$

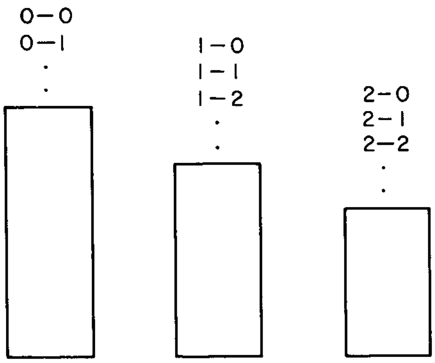
where $\tilde{\nu}_{v'v''}$ is an *average* wave number between vibrational states $v'$ and $v''$. This procedure is equivalent to using the simplified spectral model shown in Fig. 3b, as compared with the more detailed smoothed rotational model illustrated in Fig. 3a (also see Fig. 4). Then, using Eq. (29), the intensity per molecule for the complete electron transition becomes



(a) SMOOTHED ROTATIONAL MODEL



(b) FIRST VIBRATIONAL MODEL



(c) SECOND VIBRATIONAL MODEL

**Fig. 3. Schematic spectra for three molecular band models**

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 \frac{f^{elec}_{em} F'_{e,T}}{Q'_v} \times \sum_{v'} \sum_{v''} q_{v'v''} \exp\left(-\frac{E'_v}{kT}\right) \tilde{\nu}^3_{v'v''} \tag{32}$$

or alternatively, from Eq. (30)

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 f^{elec}_{abs} \frac{F''_{e,T} Q'_J}{Q''_J Q''_v} \exp\left(-\frac{hc\tilde{\nu}_{00}}{kT}\right) \times \sum_{v'} \sum_{v''} q_{v'v''} \exp\left(-\frac{E'_v}{kT}\right) \tilde{\nu}^3_{v'v''} \tag{33}$$

It is comparatively simple to use these formulas to calculate the total intensity; since it is not necessary to consider all $J$-values, as in Eqs. (29) and (30); nor is it necessary to perform a numerical or graphical integration, as in the smoothed rotational model. The result of Eq. (33) for the CN violet transition is given in Table 1.

## IV. The Second Vibrational Model

As a further simplification, suppose that to sufficient accuracy we can group the lines from a given upper vibrational state $v'$ around some average wave number $\tilde{\nu}_{v'}$. That is,

$$\sum_{v''} q_{v'v''} \tilde{\nu}^3_{v'v''} = \tilde{\nu}^3_{v'} \sum_{v''} q_{v'v''} = \tilde{\nu}^3_{v'} \tag{34}$$

using the sum rule

$$\sum_{v''} q_{v'v''} = 1$$

for the Franck-Condon factors. From Eqs. (32) and (34) one can then write

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 f^{elec}_{em} \frac{F'_{e,T}}{Q'_v} \times \sum_{v'} \tilde{\nu}^3_{v'} \exp\left(-\frac{E'_v}{kT}\right) \tag{35}$$

or alternatively, using Eq. (33)

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 f^{elec}_{abs} F''_{e,T} \frac{Q'_J}{Q''_J Q''_v} \times \exp\left(-\frac{hc\tilde{\nu}_{00}}{kT}\right) \sum_{v'} \tilde{\nu}^3_{v'} \exp\left(-\frac{E'_v}{kT}\right) \tag{36}$$

These formulas are clearly less accurate than those of the previous section, since it is more difficult to choose an *average* wave number $\tilde{\nu}_{v'}$. However, they provide a considerable simplification for practical calculations, since the Franck-Condon factors are not needed. Often these are, at best, only poorly known. Therefore, it may be useless to attempt a more accurate calculation than suggested by Eqs. (35) and (36). This second vibrational model corresponds to the spectral model illustrated in Fig. 3c.

## V. The Simplest Model

As a final model, we neglect structure altogether, and assume that all light from the electron transition (including all bands) is emitted at a *single* average frequency. That is, let

$$\sum_{v'} \tilde{\nu}^3_{v'} \exp\left(-\frac{E'_v}{kT}\right) = \tilde{\nu}^3_{av} \sum_{v'} \exp\left(-\frac{E'_v}{kT}\right) = \tilde{\nu}^3_{av} Q'_v \tag{37}$$

where $\tilde{\nu}_{av}$ is the *average* wave number. The intensity formulas of Eqs. (35) and (36) then become

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 f^{elec}_{em} F'_{e,T} \tilde{\nu}^3_{av} \tag{38}$$

or alternatively

$$\frac{I^{e'\to e''}}{N} = 4\pi \cdot 2hc^2\pi r_0 f^{elec}_{abs} F''_{e,T} \frac{Q'_J Q'_v}{Q''_J Q''_v} \exp\left(-\frac{hc\tilde{\nu}_{00}}{kT}\right) \tilde{\nu}^3_{av} \tag{39}$$

This monochromatic approximation is essentially that introduced in Ref. 5. It is the simplest, but least accurate of the models, because it is difficult to choose the proper value of $\tilde{\nu}_{av}$. If a spectrum is not too diffuse, the value can be guessed, or simply chosen to be $\tilde{\nu}_{av} = \tilde{\nu}_{00}$ as defined in Fig. 1. This value was used for the CN violet transition, and the result is given in Table 1.

## VI. Discussion

An advantage of the simpler models is that they can be quite readily calculated by hand. Besides, the poorly known oscillator strengths, the Franck-Condon factors, or the rotational constants may make more elaborate calculations pointless. However, one would like to know how to estimate the accuracy of the various models. Therefore, they were all programmed to provide direct comparisons in specific cases. In particular, each method has been used to compute the total intensity per molecule of CN violet radiation, corresponding to the $B^2\Sigma \to X^2\Sigma$ transition. The results are shown in Table 1.

**Table 1. Total band CN violet radiation at $T = 7000°$K**

| $I/N \times 10^{14}$, W/molecule | | | | |
|---|---|---|---|---|
| Simple model | Second vibrational model | First vibrational model | Smoothed rotational model | *Exact* model |
| 1.87 | 2.18 | 2.16 | 2.19 | 2.20 |

The oscillator strength used was $f^{elec}_{abs} = 0.027$, as reported in Ref. 6. The Franck-Condon factors were taken from Ref. 7, and the other molecular parameters are from Ref. 1. In the simplest model as derived in Section V, the $\tilde{\nu}_{av}$ value was chosen to be $\tilde{\nu}_{00}$, as defined in Fig. 1, rather than attempt to estimate an average wave number. Similarly, for the second vibrational model, $\tilde{\nu}_{v'}$ was chosen to be the wave number of the $v' = v''$ transitions, and for the first vibrational model, $\tilde{\nu}_{v'v''}$ was chosen to be $\tilde{\nu}^{v'v''}_0$ as used in Eq. (22).

The smoothed rotational model provides an actual detailed spectral distribution. The computer found the intensity as a function of wavelength, a sample of which is shown in Fig. 4. The spectrum was then integrated to obtain the total intensity. Finally, the total radiation was calculated by directly evaluating the sums in Eq. (30). This latter result is quoted in the last column of Table 1. It will be observed from the table that there is good agreement between the models, even for the simplest model, indicating that it would have been adequate for many applications to use one of the simpler models to find the total intensity.

Figure 5 shows the spectral distribution obtained in the first vibrational model, and compares it with an *exact* calculation using Eq. (21). The results of the latter computation were smeared out to give a continuous spectrum. As shown in the figure, the first vibrational model provides only a rough idea of local features, but the model gives a good result for the total integrated intensity, as Table 1 indicates.

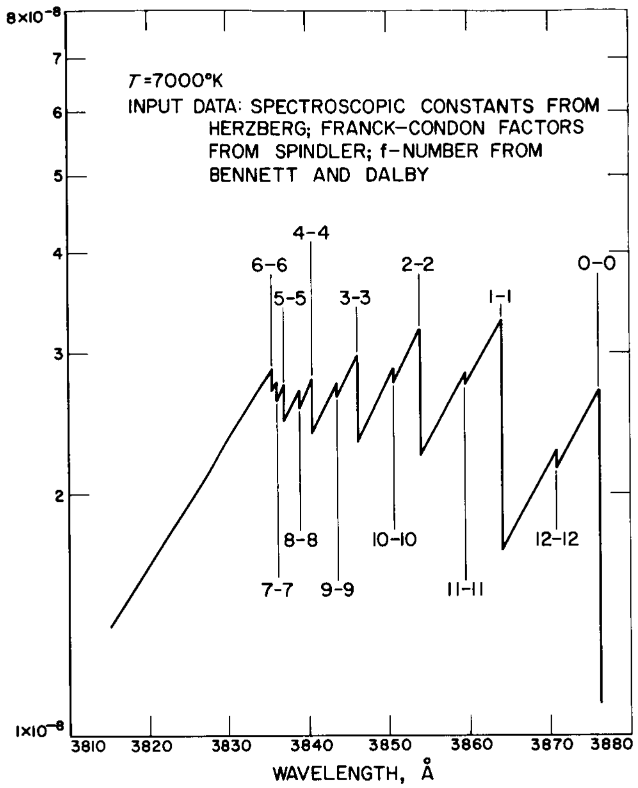


**Fig. 4. CN violet bands calculated with the smoothed rotational model (individual v′–v″ bands are identified)**

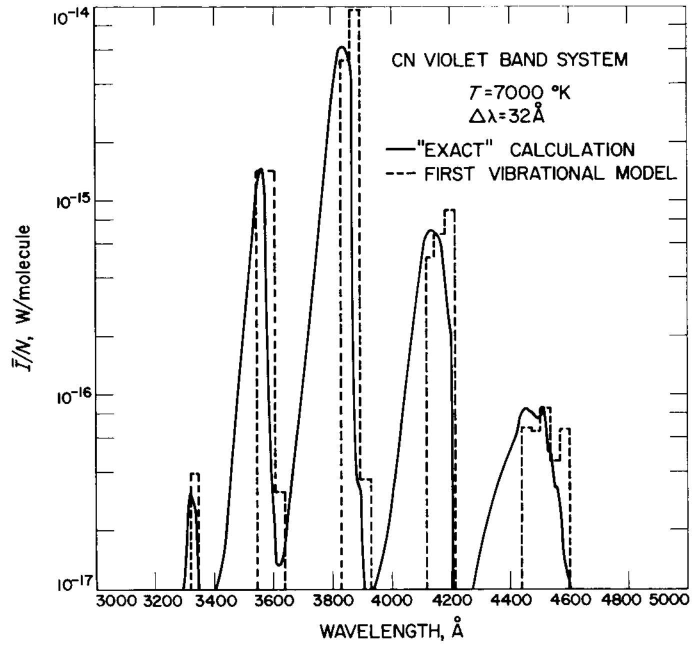


**Fig. 5. Comparison of two molecular band models**

## References

1. Herzberg, G., *Molecular Spectra and Molecular Structure: Volume I. Spectra of Diatomic Molecules.* D. Van Nostrand Company, New Jersey, 1950.
2. Williams, M. J., and Treanor, C. E., *A Method for Calculating Diatomic Spectra Using a Digital Computer,* Report QM-1626-A-5. Cornell Aeronautical Laboratory, Inc., Buffalo, N. Y., May 1962.
3. Keck, J., Camm, J., Kivel, B., and Wentink, T., "Radiation From Hot Air," *Ann. Phys.* (N.Y.), Vol. 7, p. 1, 1959.
4. Patch, R., Shackleford, W., and Penner, S., "Approximate Spectral Absorption Coefficient Calculations for Electronic Band Systems Belonging to Diatomic Molecules," *J. Q. S. R. T.*, Vol. 2, p. 263, 1962.

## References (contd)

5. Kivel, B., and Bailey, K., *Tables of Radiation From High Temperature Air*, Research Report 21. AVCO-Everett Research Laboratory, Everett, Mass., Dec. 1957.
6. Bennett, R., and Dalby, F., "Experimental Oscillator Strength of the Violet System of CN," *J. Chem. Phys.*, Vol. 36, p. 399, 1962.
7. Spindler, R. J., "Franck-Condon Factors Based on RKR Potentials with Applications to Radiative Absorption Coefficients," *J. Q. S. R. T.*, Vol. 5, p. 165, 1965.