AD722696

84130-39-T(I)

INVESTIGATIONS OF FUNDAMENTAL LASER PROCESSES

Vol I: Computation of Vibration-Rotation Matrix Elements for Diatomic Molecules

R. E. MEREDITH
F. G. SMITH

DDC
MAY 11 1971

May 1971

INFRARED AND OPTICS LABORATORY
William Ross Laboratories
INSTITUTE OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF MICHIGAN 1817

Sponsored by the Advanced Research Projects Agency,
Department of Defense, Washington, D. C.
ARPA Order No. 236, Amendment 38

Contract DAHC-15-67-C-0062

This document has been approved for public release and sale;
its distribution is unlimited.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

35

ACCESSION for
CFSTI WHITE SECTION
DDC BUFF SECTION
UNANNOUNCED
JUSTIFICATION
BY
DISTRIBUTION/AVAILABILITY CODES
DIST. AVAIL. and/or SPECIAL
A

NOTICES

Sponsorship. The work reported herein is a part of the research under BAMIRAC (Ballistic Missile Radiation Analysis Center) conducted at the Willow Run Laboratories of the Institute of Science and Technology for the Advanced Research Projects Agency, Department of Defense, Washington, D. C., under Contract DAHC-15-67-C-0062, ARPA Order 236, Amendment 38. Contracts and grants to The University of Michigan for the support of sponsored research are administered through the Office of the Vice-President for Research.

BAMIRAC. The Ballistic Missile Radiation Analysis Center is specifically concerned with electromagnetic radiation emanating from or caused by ICBM's or IRBM's in the powered and ballistic phases. In accordance with DoD Instruction 5100.45, BAMIRAC collects, processes, and disseminates information obtained from reports of field measurements and from laboratory and theoretical studies. In addition, it conducts its own theoretical and experimental investigations. BAMIRAC provides for visits of qualified persons and prepares bibliographies on request. Also, the facility aids ARPA by planning and conducting various technical conferences. This report represents one phase of the research being carried out as part of the BAMIRAC technical effort.

BAMIRAC is under the technical direction of the Infrared and Optics Division of Willow Run Laboratories, a unit of The University of Michigan's Institute of Science and Technology. It draws also upon the capabilities of the Computation Department of Willow Run Laboratories, and upon those of the Department of Aerospace Engineering and of other departments of The University of Michigan, particularly within the College of Engineering.

Distribution. Initial distribution of this report has been approved by the Advanced Research Projects Agency and is indicated at the end of this report.

Final Disposition. After this document has served its purpose, it may be destroyed. Please do not return it to Willow Run Laboratories.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)* Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, Michigan	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP N/A

3 REPORT TITLE

INVESTIGATION OF FUNDAMENTAL LASER PROCESSES (I)
VOL. I: Computation of Vibration-Rotation Matrix Elements for Diatomic Molecules

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Technical Report

5 AUTHOR(S) *(First name, middle initial, last name)*

Robert E. Meredith
Fred G. Smith

6 REPORT DATE May 1971	7a. TOTAL NO OF PAGES vi + 29	7b NO. OF REFS 13
8a. CONTRACT OR GRANT NO. DAHC-15-67-C-0062 b. PROJECT NO ARPA Order No. 236 c. Amendment 38 d.	9a. ORIGINATOR'S REPORT NUMBER(S) 84130-39-T (I) 9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10 DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Department of Defense Washington, D. C.

13 ABSTRACT

Emission and absorption of radiation by diatomic molecules is reviewed, and elementary molecular theory for use in a variety of applied physics and engineering problems is presented in a semiclassical manner. A computer code for the numerical integration of the radial Schrodinger equation has been created and is documented as a subroutine of a code for the computation of the electric dipole-moment matrix elements of diatomic molecules. The effect of vibration-rotation interaction on high v-J matrix elements is discussed.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Vibration-rotation matrix						
Diatomic molecules						
Molecular theory						
Dipole-moment matrix elements						
v-J matrix elements						

84130-39-T(I)

INVESTIGATIONS OF FUNDAMENTAL LASER PROCESSES

Vol I: Computation of Vibration-Rotation Matrix Elements for Diatomic Molecules

R. E. MEREDITH
F. G. SMITH

May 1971

Infrared and Optics Laboratory
Willow Run Laboratories
INSTITUTE OF SCIENCE AND TECHNOLOGY
THE UNIVERSITY OF MICHIGAN
Ann Arbor, Michigan

DDC
MAY 11 1971

ABSTRACT

Emission and absorption of radiation by diatomic molecules is reviewed, and elementary molecular theory for use in a variety of applied physics and engineering problems is presented in a semiclassical manner. A computer code for the numerical integration of the radial Schrodinger equation has been created and is documented as a subroutine of a code for the computation of the electric dipole-moment matrix elements of diatomic molecules. The effect of vibration-rotation interaction on high v-J matrix elements is discussed.

CONTENTS

Abstract iii

Figures vi

1. Introduction 1

2 Definitions 1
   2.1. The Absorption Process 1
   2.2. Molecular Theory 4

3. Evaluation of the Matrix Elements 7

4. The Matrix-Element Program 12

Appendix I: Evaluation of the Angular Dependent Matrix Elements 15

Appendix II: Listing of the SSM Code 19

References 28

Distribution List 29

FIGURES

1. Radiant Intensity Transmitted Through a Cell of Length x 1
2. Relative Coordinates for a Diatomic Molecule 4
3. Orientation of a Diatomic Molecule in the Laboratory Frame (θ, ϕ) 5
4. Zeroth Order Energy Levels and Band Structure of a Diatomic Molecule . . 6
5. V(r) for a Diatomic Molecule (Schematic) 8
6. Morse Potential Functions As a Function of J in the Born-Oppenheimer Approximation 9
7. Molecular Wave Functions Generated by SCHR 10

INVESTIGATIONS OF FUNDAMENTAL LASER PROCESSES

Vol I: Computation of Vibration-Rotation Matrix Elements for Diatomic Molecules

1 INTRODUCTION

The molecular parameters most important to the design of chemical laser systems and to the interpretation of chemical kinetic information are the electric dipole matrix elements of high v-J molecular transitions. Recently, matrix elements have been calculated analytically with the perturbation theory for both the harmonic oscillator [1, 2] and for the Pekeris oscillator [3]. Adequate agreement with experiment has been found for transitions involving low vibrational and rotational levels [4, 5]. However, perturbation methods do not apply to high vibrational and rotational states, since these methods neglect the extensive effects of the interaction of vibration and rotation. In many applications, exact numerical computation is necessary in order to achieve the accuracy required.

In Section 2, the absorption and emission process is discussed; the radial Schrodinger equation is presented; and the electric dipole matrix element is defined. The matrix elements are evaluated in Section 3, and Section 4 includes a description of the computer code for the numerical integration of the matrix elements. The angular matrix elements are evaluated in Appendix I. Appendix II presents a listing of the matrix-element calculation computer code.

2 DEFINITIONS

2.1. THE ABSORPTION PROCESS

Consider electromagnetic radiation of frequency f (Hz) passing through an absorption cell of length x (cm) is shown in Fig. 1. The intensity of the radiation entering the absorbing gas is $I_0(f)$ ergs/(cm^2-sec). At any point within the cell, the intensity is I(f). By Lambert's law, the loss in the intensity of the radiation, when it passes through an element, dx, is

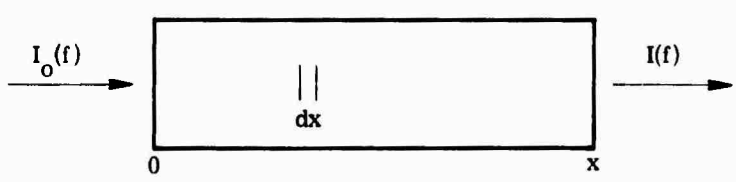

FIGURE 1. RADIANT INTENSITY TRANSMITTED THROUGH A CELL OF LENGTH x

$$dI(f) = -k(f)I(f)dx \tag{1}$$

$$I(f) = I_0(f)e^{-k(f)x} \tag{2}$$

where k(f) is a frequency-dependent function called the absorption coefficient. If the absorption occurs because of a transition from a lower, discrete level, i, to an upper discrete level, k, the absorption coefficient is written as

$$k(f) = S_{ki}F(f - f_{ki}) \tag{3}$$

where S_{ki} is a number designating the strength of the transition; f_{ki} is the center frequency of the line; and, F is a function of frequency which describes the spread of the absorbed radiation about the center frequency, f_{ki}. F is the line shape of the transition. Its form depends on the process perturbing the levels and thereby spreading them out. For example, if collision processes dominate, the shape for near infrared lines is Lorentz.

$$F(f) = \frac{\gamma}{\pi\left[(f - f_{ki})^2 + \gamma^2\right]} \tag{4}$$

where γ is the half width at the half height of k(f) [1].

Infrared spectroscopists generally describe the electromagnetic spectrum by wave number, ν (i.e., the number of wavelengths, λ, in a centimeter), in units 1/cm. Conversion factors between wave numbers, hertz, micrometers, angstroms, ergs, and kilocalories are

$$\nu(\mathrm{cm}^{-1}) = f/c$$

$$\nu(\mathrm{cm}^{-1}) = 10^{+8}/\lambda(\mathring{A})$$

$$\nu(\mathrm{cm}^{-1}) = 10^{4}/\lambda(\mu\mathrm{m})$$

$$\nu(\mathrm{cm}^{-1}) = E(\mathrm{ergs})/hc \approx 5.035 \times 10^{15}\ E(\mathrm{ergs})$$

$$\nu(\mathrm{cm}^{-1}) = 1.2028 \times 10^{5}\ E(\mathrm{kcal})$$

where f = frequency in hertz
c = speed of light
E = energy
h = Planck's constant

The strength of a line is determined spectroscopically by measuring the area under the absorption coefficient. Since the shape factor, $F(\nu - \nu_{ki})$, is normalized to unity

$$\int_{\mathrm{line}} k(\nu - \nu_{ki})d\nu = S_{ki}\int_{\mathrm{line}} F(\nu - \nu_{ki})d\nu = S_{ki} \tag{5}$$

where ν_{ki} = line center in wave numbers

The quantum mechanical expression for line strength is given by

$$S_{ki} = \frac{8\pi^3 \nu_{ki} N_i}{3hg_i c}\left[1 - e - \left(\frac{\nu_{ki} hc}{kT}\right)\right] |<\vec{\mu}(r, \theta, \phi)>_{ki}|^2 \tag{6}$$

where T = temperature

k = Boltzmann's constant

N_i = the number of molecules per cubic centimeter occupying the lower level

g_i = the statistical weight factor for the energy level i

The quantity $<\vec{\mu}(r, \theta, \phi)>_{ki}$ is the quantum mechanical average of the electric dipole moment $\vec{\mu}(r, \theta, \phi)$ between the levels k and i. More will be said of $<\vec{\mu}(r, \theta, \phi)>_{ki}$ in the following section.

The $<\vec{\mu}(r, \theta, \phi)>_{ki}$ is related to the Einstein transition probabilities so that

$$B_{ki} = \frac{32\pi^4}{3h^2 c g_k} |<\vec{\mu}(r, \theta, \phi)>_{ki}|^2 \left(\frac{cm^2}{\text{molecule-erg-sec}}\right) \tag{7}$$

$$B_{ik} = \frac{g_k}{g_i} B_{ki} \left(\frac{cm^2}{\text{molecule-erg-sec}}\right) \tag{8}$$

$$A_{ki} = \frac{64\pi^4 \nu_{ki}^3}{3hg_k} |<\vec{\mu}(r, \theta, \phi)>_{ki}|^2 \quad 1/\text{sec} \tag{9}$$

$$A_{ki} = 8\pi\nu_{ki}^3 h B_{ki}$$

where B_{ki} = the transition probability for induced emission of wave number ν_{ki}

B_{ik} = the transition probability for induced absorption of wave number ν_{ik}

A_{ki} = the transition probability for spontaneous emission of wave number ν_{ki}

g_k = statistical weight

$<\vec{\mu}(r, \theta, \phi)>_{ki}$ = units esu-cm, where 1 esu = $\sqrt{\text{erg}\cdot\text{cm}}$

Intensity rather than energy-density Einstein coefficients are used. That is,

$$B_{ki}(\text{intensity}) = \frac{4\pi}{c} B_{ki}(\text{energy density})$$

The inclusion of 4π in these relations implies radiation into a hemisphere, rather than into a unit solid angle. Hence, the units of B_{ki} are not per steradian.

2.2. MOLECULAR THEORY

The internal motion of a diatomic molecule is best described by the relative coordinate r, defined in Fig. 2. The rotational energy (E_R) of the molecule is given as

$$E_R = \frac{1}{2} I\omega^2$$

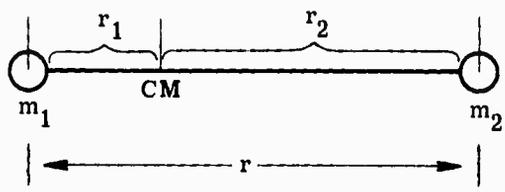

FIGURE 2. RELATIVE COORDINATES FOR A DIATOMIC MOLECULE

where ω is the rotational frequency, and I is the moment of inertia. Since the rotation axis passes through the center of mass,

$$I = \sum_i r_i^2 m_i = m_1 r_1^2 + m_2 r_2^2 \tag{10a}$$

where m_1 and m_2 are the masses of the two atoms. The moment of inertia may be written in terms of a reduced mass m

$$I = mr^2 \tag{10b}$$

where

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

For descriptive purposes, it is apparent that the molecule can be described by a point mass of value m a distance r from the origin, as shown in Fig. 3, where κ_{ej} are the electronic coordinates. If it is assumed that the electronic, vibrational and rotational motions are independent, a function $\psi(r, \theta, \phi)$ may be written as a product of functions of a single coordinate [6]:

$$\begin{aligned} \psi(r, \theta, \phi) &= R(r) P_J^M(\cos\theta) e^{iM\phi} \\ \psi(r, \theta, \phi) &= R(r) Y_J^M(\theta, \phi) \end{aligned} \tag{11}$$

where J and M are quantum numbers specifying the total augular momentum of the molecule and its projection on a direction fixed in space and P_J^M = a Legendre polynomial. $Y_J^M(\theta, \phi)$ are

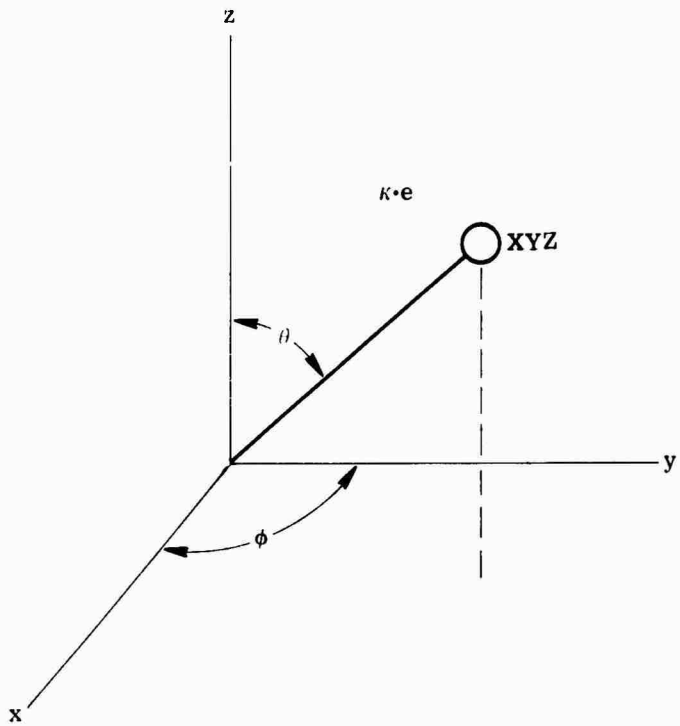

FIGURE 3. ORIENTATION OF A DIATOMIC MOLECULE IN THE LABORATORY FRAME (θ, ϕ)

associated Legendre polynomials. The functions R(r) are solutions of the radial Schrodinger equation

$$\frac{d^2U(r)}{dr^2} + \frac{8\pi^2 m}{h^2}\left[E - V(r) - \frac{h^2}{8\pi^2 m r^2}J(J+1)\right]U(r) = 0 \tag{12}$$

where $U(r) \equiv rR(r)$ and E is the internal energy of the molecule and assumes discrete values. V(r) is the potential energy of the molecule. To a low order of approximation, the nuclear motion may be assumed to be harmonic $\left(\text{i.e., } V(r) \cong -k(r - r_e)^2/2\right)$, and the term $J(J + 1)/r^2$ may be replaced by $J(J + 1)/r_e^2$. For this approximation, the internal energy for the ground electronic state is the sum, E, of vibrational and rotational energies

$$E = \omega_e(v + 1/2) + B_e J(J + 1) \tag{13}$$

where ω_e and B_e are spectroscopic constants in wave-number units, and v is the vibrational quantum number. Absorption and emission occur between two levels labeled v'J' and vJ, resulting in a band structure shown in Fig. 4. Transitions are allowed only between levels so that $\Delta J = J' - J = \pm 1$. The transitions that occur in the smaller wave-number side of the band cen-

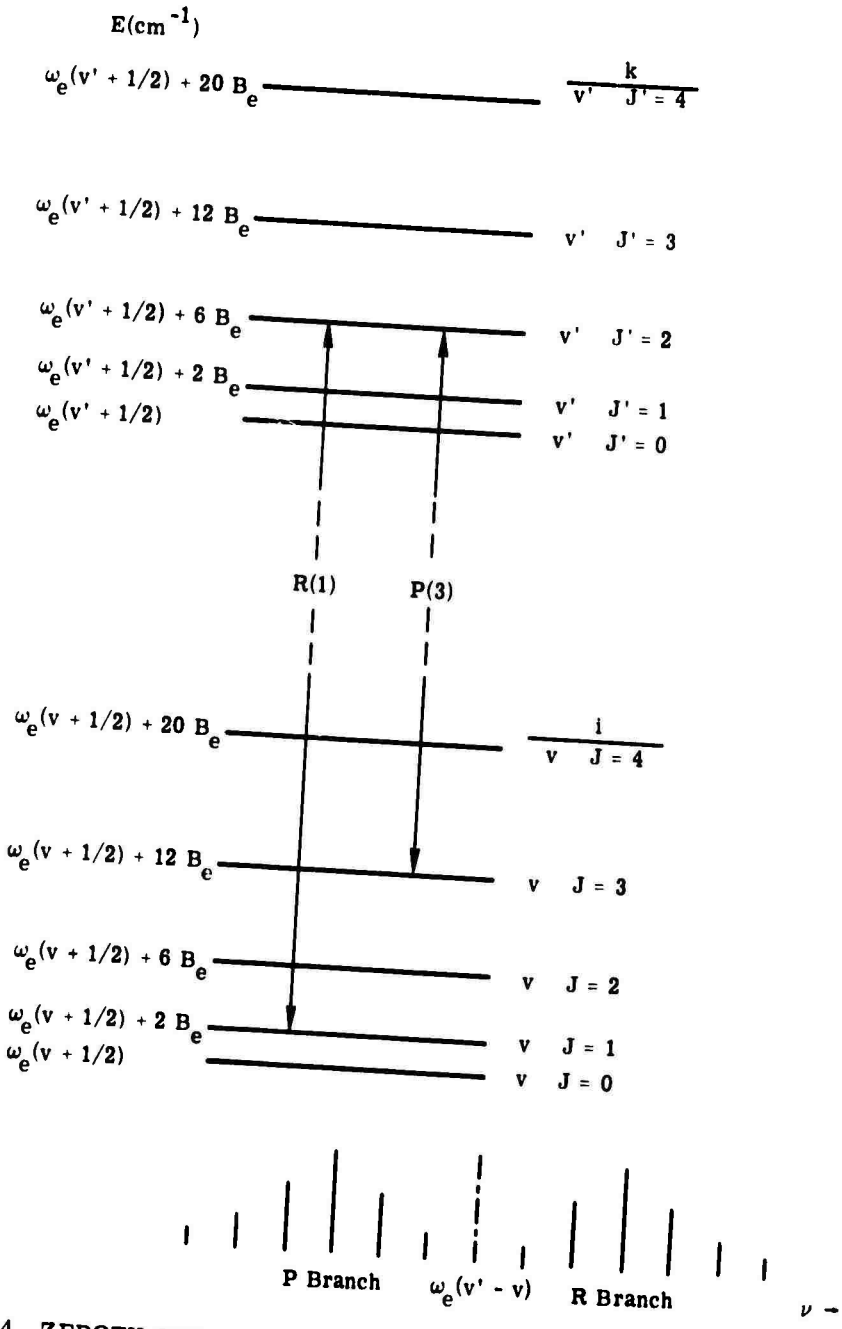

FIGURE 4. ZEROTH ORDER ENERGY LEVELS AND BAND STRUCTURE OF A DIATOMIC MOLECULE

ter ($\Delta J = -1$) are called P branch lines, and those on the larger wave-number side ($\Delta J = +1$) are called R branch lines. A more realistic model for the potential function produces important quantitative differences in the energy-level scheme and band structure; but the qualitative features are unchanged. For a given energy level, the label i then becomes $i \longleftrightarrow (v, J)$, and the wave function is written $\psi_{vJ}(r, \theta, \phi)$. The significance of $\psi_{vJ}(r, \theta, \phi)$ is that the product $\psi^*_{vJ}(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi)$ is the probability that the molecule will be oriented at the angles θ, ϕ and that the nuclear separation will be r. Since the molecule exists somewhere in space, $\psi_{vJ}(r, \theta, \phi)$ is normalized to

$$\iiint_{\text{space}} \psi^*_{vJ}(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi) r^2 \sin\theta \, dr \, d\theta \, d\phi = 1 \tag{14}$$

As a shorthand notation, the symbol $|vJ\rangle$ is introduced

$$|vJ\rangle \equiv \psi_{vJ}(r, \theta, \phi)$$

$$\langle vJ| \equiv \psi^*_{vJ}(r, \theta, \phi)$$

and the integral over the coordinates of the product of two functions are written as

$$\langle vJ|vJ\rangle = \iiint_{\text{space}} \psi^*_{vJ}(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi) r^2 \sin\theta \, dr \, d\theta \, d\phi \tag{15}$$

This notation is extended to include integrals which encompass a third function

$$\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle = \iiint_{\text{space}} \psi^*_{v'J'}(r, \theta, \phi)\vec{\mu}(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi) r^2 \sin\theta \, dr \, d\theta \, d\phi \tag{16}$$

The quantities $\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle$ form the elements of a matrix for arbitrary vJ and v'J' and are called matrix elements. Equation (16) is the definition of the electric dipole matrix elements. The magnitude of the matrix element $\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle$ determines the transition probabilities for absorption and emission between levels $v'J' \longleftrightarrow vJ$, according to Eqs. (7), (8), and (9). That is, since the J levels are degenerate in M

$$\langle \vec{\mu}(r, \theta, \phi)\rangle_{ki} = \sum_{M,M'} \langle v'J'M'|\vec{\mu}(r, \theta, \phi)|vJM\rangle \tag{17}$$

3
EVALUATION OF THE MATRIX ELEMENTS

Accurate evaluation of matrix elements for even moderately large v and J requires realistic models for the mechanical potential function V(r) and requires that the vibration-rotation interaction $J(J+1)/r^2 \approx J(J+1)/r_e$ be taken into account when the $\psi(r, \theta, \phi)$ are evaluated. The

general shape of a potential function for a given J is shown in Fig. 5. The contour represents the minimum and maximum separation of the nuclei (i.e., the turning points of the classical motion). D_e is the dissociation energy. Each line in the well represents a possible vibrational energy for a given value of J. Near the bottom of the well, where the oscillations are small, the form of V(r) is more nearly parabolic, and the harmonic oscillator approximation is useful. For moderate v, the details of the well must be known for quantitative work. The appearance of $J(J + 1)/r^2$ in the Schrodinger equation results in an effective potential energy which, as Fig. 6 illustrates, raises the potential well for the lower portion of a Morse potential,

$$V_{eff}(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2 + \frac{h^2}{8\pi^2 m}\left[\frac{J(J+1)}{r^2}\right] \tag{18}$$

Wave functions which we computed numerically from Eq. (12), using the Morse potential and including the vibration-rotation interaction, are shown in Fig. 7. The ordinate in Fig. 7 is the dimensionless energy unit $E = \frac{mE(cm^{-1})}{60.219}$.

A realistic model of the electric dipole moment must be established. Let $\vec{\mu}(r, \theta, \phi)$ be the dipole-moment function described in the laboratory frame. The moment fixed in the molecule (μ_F) has a component only along the internuclear axis (Fig. 3). μ_F depends on the electric

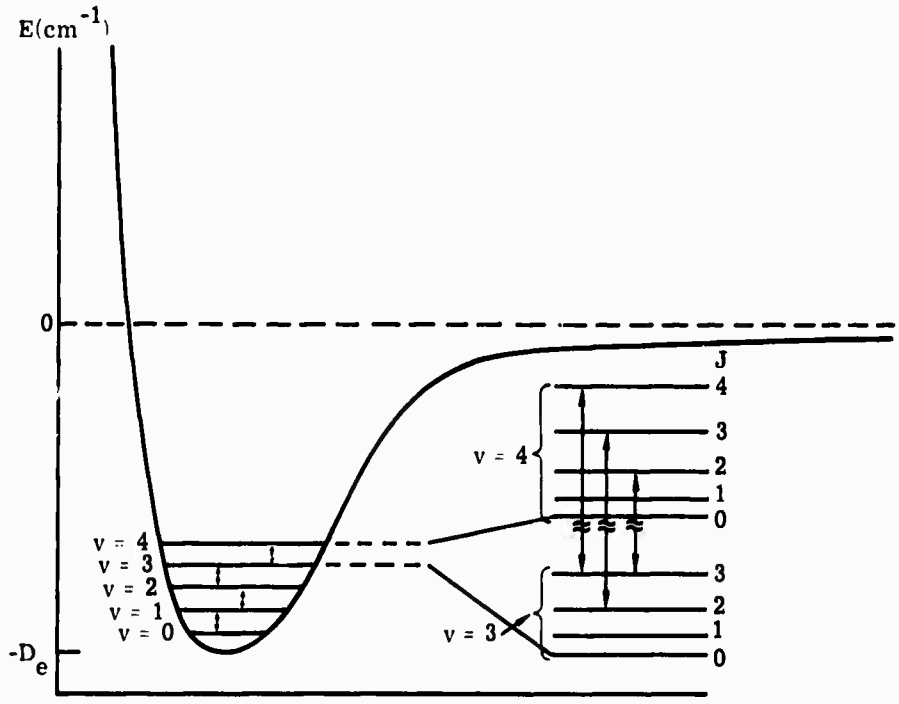

FIGURE 5. V(r) FOR A DIATOMIC MOLECULE (SCHEMATIC)

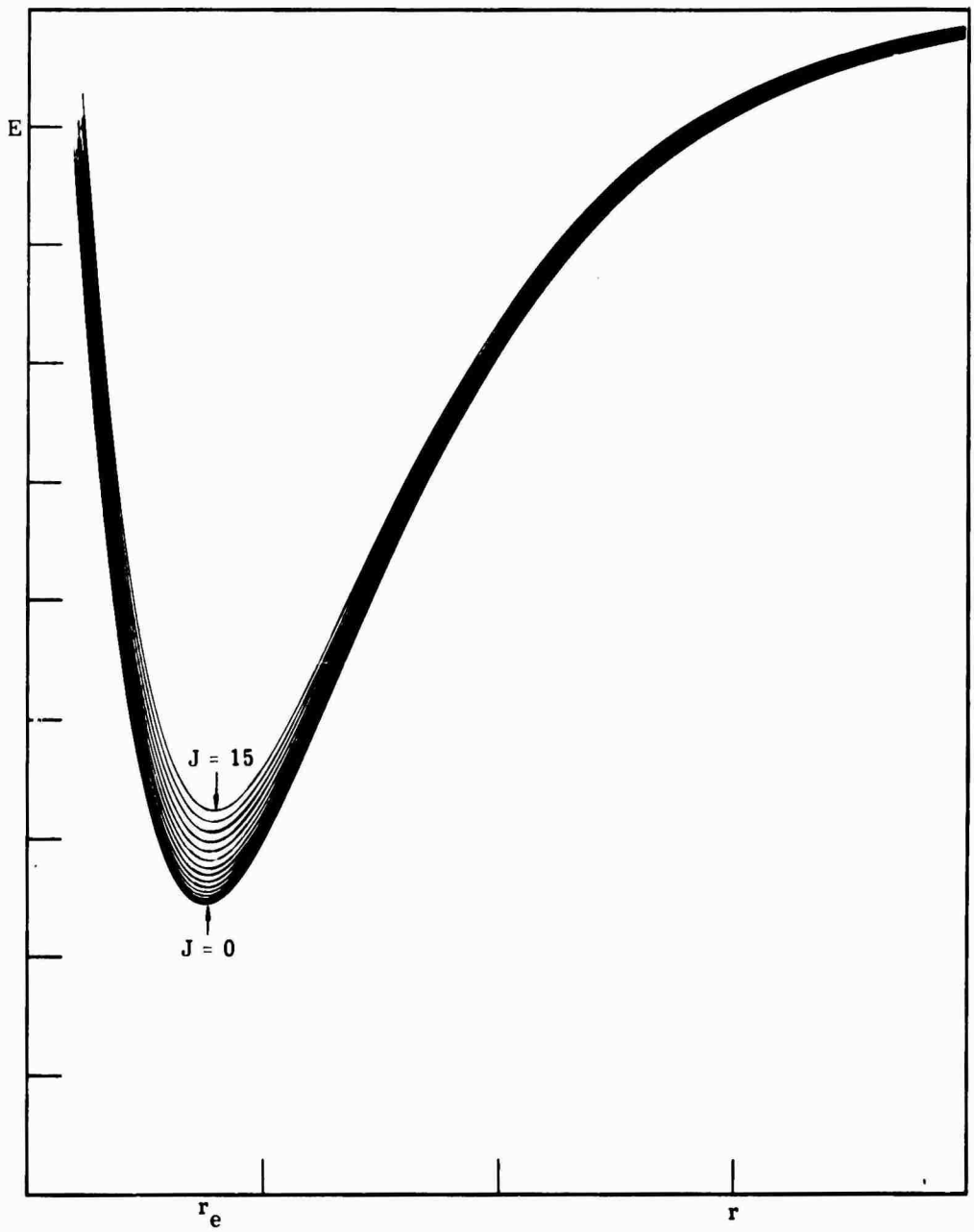

FIGURE 6. MORSE POTENTIAL FUNCTIONS AS A FUNCTION OF J IN THE BORN-OPPENHEIMER APPROXIMATION

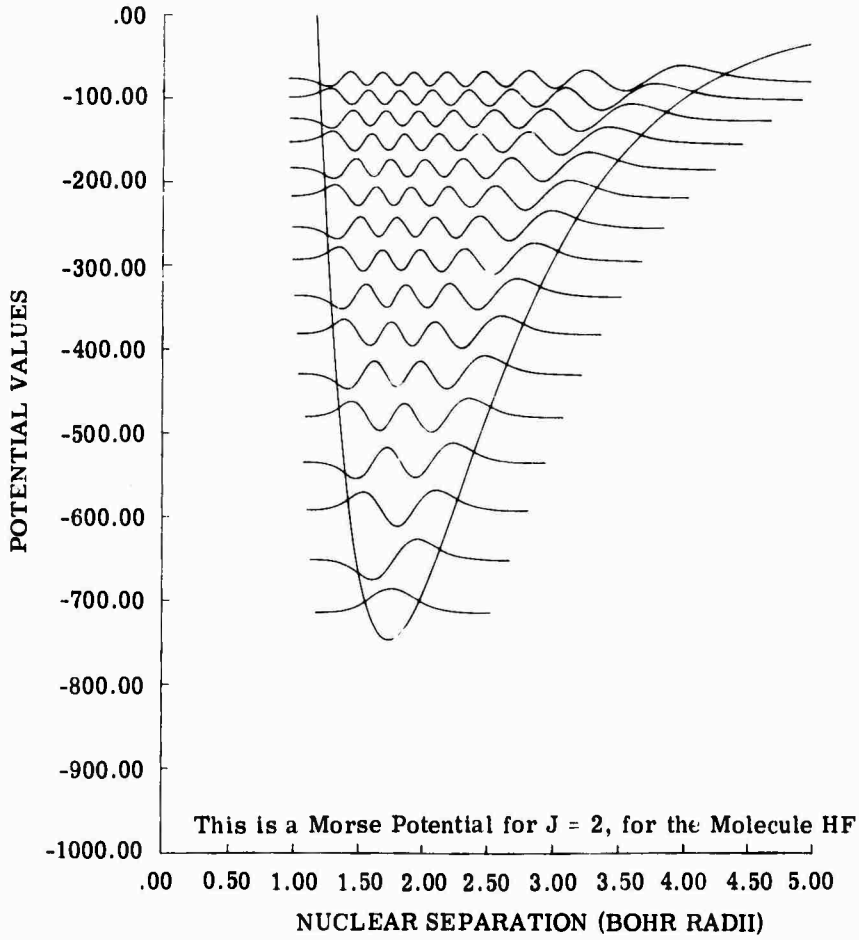

FIGURE 7. MOLECULAR WAVE FUNCTIONS GENERATED BY SCHR

charge distribution and motion, and it may be described by a coordinate system fixed in the molecule

$$\mu_F = -e\sum_i z_i + \sum_j eZ_j \tag{19}$$

where the coordinates are relative to axes fixed in the molecule. z_i refers to the electronic coordinates, and Z_j refers to nuclear coordinates. If κ equals the coordinates which describe the charge distribution

$$\mu_F \equiv \mu(\kappa)$$

From Fig. 3, the vector $\vec{\mu}(r, \theta, \phi) = (\mu_x, \mu_y, \mu_z)$ may be written as a product of μ_F, the molecule fixed dipole-moment function, and the direction cosines

$$\mu_x = \mu_F(\kappa)\cos(x, Z) = \mu_F(\kappa)\sin\theta\cos\phi$$

$$\mu_y = \mu_F(\kappa)\cos(y, Z) = \mu_F(\kappa)\sin\theta\sin\phi \tag{20}$$

$$\mu_z = \mu_F(\kappa)\cos(z, Z) = \mu_F(\kappa)\cos\theta$$

The matrix elements of $\mu_x(r, \theta, \phi)$ are

$$\langle v', J', M', n'|\mu_x|v, J, M, n\rangle = \int d\kappa \iiint dr r^2 \sin\theta\, d\phi\, d\theta\, \Phi_n^*(\kappa)\psi^*_{v'J'M'}(r, \theta, \phi)\mu_F \cos(x, Z) \times \Phi_n(\kappa)\psi_{vJM}(r, \theta, \phi)$$

where $\Phi_n(\kappa)$ are the electronic wave functions for the electronic state n. The term electric dipole moment, as it is used in molecular theory, generally means the electron-dependent integral. That is, $\mu(r)$ is the electric dipole moment, where

$$\mu(r) = \int d\kappa \Phi_n^*(\kappa)\mu(\kappa)\Phi_n(\kappa) \tag{21}$$

The moment is clearly dependent upon r, since μ_F and the $\Phi(\kappa)$ generally vary, as the nuclei vibrate. The matrix elements are now written as

$$\langle v'J'M'|\mu_x|vJM\rangle = \int_0^\infty dr r^2 R^*_{v'J'}(r)\mu(r)R_{vJ}(r)\int_0^\pi\int_0^{2\pi} d\theta \sin\theta\, d\phi(\sin\theta\cos\phi)Y_{J'}^{*M'}(\theta, \phi)Y_J^M(\theta, \phi)$$

$$\langle v'J'M'|\mu_y|vJM\rangle = \int_0^\infty dr r^2 R^*_{v'J'}(r)\mu(r)R_{vJ}(r)\int_0^\pi\int_0^{2\pi} d\theta \sin\theta\, d\phi(\sin\theta\sin\phi)Y_{J'}^{*M'}(\theta, \phi)Y_J^M(\theta, \phi)$$

$$\langle v'J'M'|\mu_z|vJM\rangle = \int_0^\infty dr r^2 R^*_{v'J'}(r)\mu(r)R_{vJ}(r)\int_0^\pi\int_0^{2\pi} d\theta \sin\theta\, d\phi(\cos\theta)Y_{J'}^{*M'}(\theta, \phi)Y_J^M(\theta, \phi) \tag{22}$$

or

$$\langle v'J'M'|\mu_x|vJM\rangle = \langle v'J'|\mu(r)|vJ\rangle\langle J'M'|\sin\theta\cos\phi|JM\rangle$$

$$\langle v'J'M'|\mu_y|vJM\rangle = \langle v'J'|\mu(r)|vJ\rangle\langle J'M'|\sin\theta\sin\phi|JM\rangle$$

$$\langle v'J'M'|\mu_z|vJM\rangle = \langle v'J'|\mu(r)|vJ\rangle\langle J'M'|\cos\theta|JM\rangle \tag{23}$$

The angular integrals are found by standard techniques. (See Appendix I.) The results are:

$$|\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle|^2 = \sum_{MM'}\Big(|\langle v'J'M'|\mu_x|vJM\rangle|^2 + |\langle v'J'M'|\mu_y|vJM\rangle|^2 + |\langle v'J'M'|\mu_z|vJM\rangle|^2\Big) \tag{24}$$

$$|\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle|^2 = (J+1)\int_0^\infty R(r)\mu(r)R(r)r^2\,dr \qquad \text{R Branch}$$

$$= (J)\int_0^\infty R(r)\mu(r)R(r)r^2\,dr \qquad \text{P Branch} \tag{25}$$

or, rewriting the integral in the matrix element notation

$$|\langle v'J'|\vec{\mu}(r, \theta, \phi)|vJ\rangle|^2 = |\langle v'J'|\mu(r)|vJ\rangle|^2 \begin{cases} J+1 & \text{R Branch} \\ J & \text{P Branch} \end{cases} \tag{26}$$

4
THE MATRIX-ELEMENT PROGRAM

Presently in use is a program to generate numerically the $\langle v'J'|\mu(r)|vJ\rangle$ matrix elements which appear in Eq. (26) of the preceding section. A listing of that program is given in Appendix II. In order to calculate these matrix elements, three separate calculations must be performed. First, the radial Schrodinger Eq. (12) must be solved in order to obtain the radial wave functions for the initial and final states. Next, the dipole-moment function $\mu(r)$ must be generated. Finally, the integral appearing in Eq. (25) must be numerically calculated. The calling program to handle these calculations is SSM.

Before the Schrodinger equation can be solved, some potential function must be assumed. The SSM program provides for three types of potential functions: the Morse; Dunham; and Rydberg, Klein, Rees [7, 8, 9] (RKR) potentials. The Morse potential, β, can be generated from the low-order spectroscopic constants of the molecule and has the form

$$V(r) = \frac{\omega_e^2}{4\cdot\omega_e x_e}(1 - e^{-2\beta\xi})^2$$

with

$$\beta = \left(\frac{\omega_e x_e}{4\beta_e}\right)^{1/2}$$

and

$$\xi = \frac{r - r_e}{r_e}$$

where ξ is the dimensionless molecular coordinate and ω_e and $\omega_e x_e$ are spectroscopic constants. The Dunham potential has the form of a power-series expansion:

$$V(r) = \sum_{i=0}^{n} a_i \left(\frac{r - r_e}{r_e} \right)^i$$

where the a_i are constants related to the spectroscopic constants. The RKR potential is also found from the energy levels of the molecule. However, the procedure is quite complicated. In the program, this potential can be entered as a number of energy values tabulated at various nuclear separations, r. The program uses a third-degree polynomial interpolation to calculate the potential at the points necessary to obtain the differential equation solution. In spectroscopy, energy is usually expressed in wave-number units; thus, SSM has been written to accept the defining parameters in those units. However, the Schrodinger equation-solution subroutine (SCHR) requires that the energy be expressed in dimensionless units, therefore, a subroutine MORSE is provided to obtain the proper, dimensionless Morse parameters. The Dunham constants must be entered directly in the dimensionless units. The conversion to the dimensionless quantities for the RKR potential is handled internally by SSM.

The solution of the radial Schrodinger equation is accomplished by the SCHR subroutine. The SCHR subroutine is patterned very closely after a Fortran II program, by Zare and Cashion [10, 11] who base their work on a paper by Cooley [12]. When given an initial energy estimate, the subroutine uses a three-point central difference predictor-correlator formula to generate two partial wave functions. One of these satisifies the boundary condition at small r, and the other satisfies the boundary condition for large r. The continuity of derivative of the two partial wave functions is then used to generate a new energy estimate. The iteration continues until a tolerance on the energy change is reached.

Our only significant modification to Zare and Cashion's program was the use of double precision arithmetic in the finite difference equations, the energy values, and the sum accumulations. The general accuracy of the program has been discussed elsewhere [11], but of particular interest here is the orthogonality of the calculated wave functions. Because the radial Schrodinger equation is of Strum-Liouville Form for the exact wave functions, the orthogonality relation holds.

$$\int R_i(r) R_j(r) r^2 \, dr = 0 \quad i \neq j$$

where R_i and R_j are arbitrary radial molecular wave functions. Values of similar integrals evaluated by SSM for the numerically generated wave functions were generally about 10^{-8} and were less than 10^{-6} in all cases.

The initial energy estimate which SCHR requires is calculated by another subroutine, MANENG, which evaluates a term expansion to obtain the approximate energy for the desired state of the molecule.

$$E(v, J) = \sum_{\ell j} Y_{\ell j}\left(v + \frac{1}{2}\right)^{\ell} [J(J + 1)]^{j}$$

The $Y_{\ell j}$ are related to the spectroscopic constants of the specific molecule under investigation.

The dipole moment is approximated as a polynomial of the form

$$\mu(r) = \sum_{i=0}^{n} M_i \left(\frac{r - r_e}{r_e}\right)^{i}$$

The M_i are related to the rotationless matrix elements, which are experimentally measured. The value of $\mu(r)$ is found at the same radial increments at which the wave functions were found by the SCHR subroutine; then it is multiplied, point by point, by the wave functions of the upper and lower states, to give the integrand of $\int R_{v'J'} \mu R_{vJ} r^2 \, dr$ at those points.

The composite trapezoidal rule is used to perform the numerical integration. Higher order integration schemes are unnecessary, since wave functions have already been generated at a large number of points in the numeric differential equation solution process. The position of the lines and the Einstein transition probability, $A_{v'J'vJ}$, are calculated and printed out after the matrix element $\langle v'J' | \mu(r) | vJ \rangle$ has been calculated.

Appendix I
EVALUATION OF THE ANGULAR DEPENDENT MATRIX ELEMENTS

It is a postulate of the quantum theory [13] that the probability of electric dipole radiation from an upper state J'M' to a lower state JM is

$$A_{J'M',JM} = \frac{64\pi^4 f^3}{3hc^3} |\langle J'M' | \vec{\mu}(\theta, \phi) | JM \rangle|^2 \tag{27}$$

The spontaneously emitted intensity of such radiation is

$$I_{J'M',JM} = N_{J'M'} hf A_{J'M',JM} \tag{28}$$

On the other hand, the intensity of a line is the sum of the intensities of all possible transitions between the degenerate states M' and M

$$I_{J',J} = \frac{64\pi^4 f^4}{3c^3} N_{J'M'} \sum_{M'}^{g_{J'}} \sum_{M} |\langle J'M' | \vec{\mu}(\theta, \phi) | JM \rangle|^2 \tag{29}$$

In Eq. (29), the sum over the final (unprimed) states may be taken first, leaving $g_{J'}$ terms in the sum over the initial (primed) states. Equation (29) is usually written as

$$I_{J',J} = \frac{64\pi^4 f^4}{3c^3} \left(\frac{N_{J'}}{2J' + 1} \right) \sum_{M'M} |\langle J'M' | \vec{\mu}(\theta, \phi) | JM \rangle|^2 \tag{30}$$

where it is assumed that natural emission is taking place, making all the $N_{J'M'}$ equal.

The expression for the emitted intensity of radiation from a level J' to a level J is

$$I_{J',J} = N_{J'} hf A_{J',J} \tag{31}$$

where $A_{J',J}$ is the Einstein spontaneous transition probability. From Eqs. (30) and (31)

$$A_{J',J} = \frac{64\pi^4 \nu^3}{3h(2J' + 1)} \sum_{M'M} |\langle J'M' | \vec{\mu}(\theta, \phi) | JM \rangle|^2 \tag{32}$$

The sum in Eq. (32) must be unchanged by interchange of the initial and final states, whereas $A_{J',J}$ is not changed because of the factor $1/(2J' + 1)$. The sum is therefore an invariant property of the pair of levels J' and J for both emission and absorption, whereas $A_{J',J}$ is not. One must distinguish between the matrix elements, which are between $|\langle J'M'|$ and $|JM\rangle|$, and their sum, S(J', J).

$$S(J', J) = \sum_{M'M} |\langle J'M'|\vec{\mu}(\theta, \phi)|JM\rangle|^2 \tag{33}$$

S(J', J') is called the strength factor of the liue and should not be confused with the line strength S_{kj}. Its relation to the individual transitions is best seen in Eq. (29). In (29), if the sum over VM ' is carried out first, then

$$S(J', J) = (2J' + 1)\sum_{M} |\langle J'M'|\vec{\mu}(\theta, \phi)|JM\rangle|^2 \tag{34}$$

The integrals in (34) are written explicitly in Eq. (22). It can be shown that the integration over ϕ contributes the factor 1/2 to μ_x and μ_y and 1 to μ_z. Also, it may be shown that M is restricted to the values $M = M' \pm 1$ for μ_x and μ_y, and to $M = M'$ for μ_z. S(J', J) is given by

$$S(J', J) = (2J' + 1)\Big[\tfrac{1}{2}(|\langle J'M'|\sin\theta|JM' - 1\rangle|^2 + |\langle J'M'|\sin\theta|JM' + 1\rangle|^2)$$

$$+ |\langle J'M'|\cos\theta|JM'\rangle|^2\Big] \tag{35}$$

The integrals in (35) may be evaluated using the recurrence relations for associated Legendre functions:

$$(2J + 1)\cos\theta P_{J'}^{M'} = (J' - M' + 1)P_{J'+1}^{M'} + (J' + M')P_{J'-1}^{M'}$$

$$(2J' + 1)\sin\theta P_{J'}^{M'} = (J' + M')(J' + M' - 1)P_{J'-1}^{M'-1} - (J' - M' + 1)(J' - M' + 2)P_{J'+1}^{M'-1} \tag{36}$$

$$(2J' + 1)\sin\theta P_{J'}^{M'} = P_{J'+1}^{M'+1} - P_{J'-1}^{M'+1}$$

Values of J are clearly limited to $J' \pm 1$. The results are:

$$|\langle J'M'|\sin\theta|J, M' - 1\rangle|^2 = \frac{(J' + M' - 1)(J' + M')}{(2J' - 1)(2J' + 1)} \qquad J = J' - 1$$

$$|\langle J'M'|\sin\theta|J, M' - 1\rangle|^2 = \frac{(J' - M' + 2)(J' - M' + 1)}{(2J' + 1)(2J' + 3)} \qquad J = J' + 1$$

$$|\langle J'M'|\sin\theta|J, M' + 1\rangle|^2 = \frac{(J' - M' - 1)(J' - M')}{(2J' + 1)(2J' - 1)} \qquad J = J' - 1$$

$$|\langle J'M'|\sin\theta|J, M' + 1\rangle|^2 = \frac{(J' + M' + 2)(J' + M' + 1)}{(J' + 1)(2J' + 3)} \qquad J = J' + 1 \tag{37}$$

$$|\langle J'M'|\cos\theta|J, M'\rangle|^2 = \frac{(J' - M')(J' + M')}{(2J' - 1)(2J' + 1)} \qquad J = J' - 1$$

$$|\langle J'M'|\cos\theta|J, M'\rangle|^2 = \frac{(J' - M' + 1)(J' + M' + 1)}{(2J' + 1)(2J' + 3)} \qquad J = J' + 1$$

For R branch transitions ($J = J' - 1$), $S(J', J)$ is the sum of the first, third, and fifth terms in (37).

$$S(J', J) = (2J' + 1)\left(\frac{J'}{2J' + 1}\right) = J + 1 \quad \text{R branch}$$

for the P branch ($J = J' + 1$)

$$S(J', J) = (2J' + 1)\left(\frac{J' + 1}{2J' + 1}\right) = J \quad \text{P branch}$$

This is the result stated in Eq. (25).

The details of the evaluation of the matrix elements have no direct bearing on our computer program or its results. The angular dependent parts are clearly separated in advance, and the selection rules $J = \pm 1$ are built in. If quadrupole, Stark, or electric field-induced absorption or emission is to be investigated, however, the transformation properties of the particular tensor operator must be understood so the proper selection rules and strength factors may be used.

Appendix II
LISTING OF THE SSM CODE

PRECEDING PAGE BLANK

NOT REPRODUCIBLE

```
F
      COMMON P(2005),S1(2005),S2(2005),U(2005),RMAX,RMIN,N,
     1KMODES,EZERO,EPS,MAXIT
      REAL*8 SUM,P
      REAL M
      DATA K,ICK/10,0/
      DATA PPP/'PRNT'/
      REAL MUSUBA,MUCON,LAMBDA,M0,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11
      DATA M0,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11/12*0./
      DIMENSION W(200),RS(200),M(2005),VEF(2),JAY(2)
     2,SD(2005),SET(10),TYPES(9)
     3,PMAN(2),COMMI5),EMOR(2)
     4,A(4),PNAME(3)
      DATA WE,BE,RE,MUSUBA/4139.04,20.956,.9168E-8,.957347/
      DATA WEXE/90.05/
C     PKR POTENTIAL PARAMETERS
      DATA W/109894.,48294.,47292.,46031.,44543.,
     142850.,40973.,38921.,36705.,34355.,31875.,29191.,
     226350.,23351.,20193.,16878.,13419.,9798.,6008.,
     32047.,0.,2047.,6008.,9798.,13419.,16878.,20193.,
     423351.,26350.,29191.,31875.,34355.,36705.,38921.,
     540973.,42850.,44543.,46031.,47292.,48294.,49296./
      DATA RS/.5,.623,.625,.628,.631,.635,.639,.644,
     1.650,.656,.662,.670,.679,.686,.701,.716,.733,
     2.755,.786,.836,.901,1.023,1.115,1.187,1.253,
     31.317,1.379,1.441,1.503,1.567,1.633,1.701,1.772,1.847
     4,1.922,2.009,2.108,2.223,2.346,2.555,2.764/
      DATA NW/41/
      INTEGER DOJ
      DATA DOJ/0/
      DATA PNAME/'MORS','DUNH','PKR'/
      DATA SET/10*-10./
      DATA XNO/'NO  '/
      DATA TYPES/'S1  S2  M   M1  CALCPOT PTS1PTS2MOUT'/
      DATA IC,IERR,IS,QUIT/0,0,-10,'DONE'/
      INTEGER V,WHICHS,VEE
      CALL FCVTHB(5.0)
      MAXIT=10
      WRITE(2,6)
    6 FORMAT('1DO YOU NEED THE EXPLANATION ? ',
     1 ' (ENTER YES OR NO)')
      CALL SETPFX('?',1)
      READ(1,25)ANSWER
      CALL SETPFX(' ',1)
      IF(ANSWER.EQ.XNO) GO TO 15
      WRITE(2,10)
   10 FORMAT('1SSM CALCULATES THE INTEGRAL OF THE ',
     1'PRODUCT S1(I)*S2(I)*M(I) , I=1,N'/' AND STEPS ',
     2'OF H=(RMAX-RMIN)/N .  THREE POTENTIAL FUNCTIONS'/
     3' ARE AVAILABLE FOR GENERATING S1 AND S2 .'/
     4'0INDICATE THE DESIRED OPERATION BY ENTERING THE '
     5,'APPROPRIATE'/' OPERATION TYPE WHEN REQUESTED.',
     6'  THE ALLOWED TYPES ARE :'/'0"PRNT"',T10,
     6'PRINT EVERY K"TH POINT'/,T10,' OF THE FOLLOWING POTINTIALS.'/,
     6T10,' IF K.LT.0  TURN PRINT OFF.'/,' "S1  "',T10,
     7'GENERATE WAVE FUNCTION S1'/' "S2  "',T10,
     8'GENERATE WAVE FUNCTION S2'/' "M   "',T10,
     9'CALCULATE M USING M0,M1,M2,M3'/' "M1  "',T10,
     1'SET ALL M(I) = 1.0'/' "CALC"',T10,'PERFORM ',
     2'THE INTEGRATION'/' "POT "',T10,'GENERATE ',
     3'THE POTENTIAL FUNCTION'/' "PTS1"',T10,4HLIST,
     4' S1  ( EVERY K"TH )  '/' "PTS2"',T10,2X,1H",
     52X,'S2  ( POINT PRINTED )'/' "MOUT"',T12,1H",
     62X,'M   ( DEFAULT  K=10)')
```

```
      WRITE(2,11)
   11 FORMAT(' "DONE"',T10,'RETURN TO MTS')
      IC=0
      IERR=0
   15 WRITE(2,20)
   20 FORMAT('0ENTER TYPE PLEASE')
      ISTEP=0
      CALL SETPFX('?',1)
   23 READ(1,25,ERR=31)TYPE,IPP
   25 FORMAT(A4,I5)
      CALL SETPFX(' ',1)
      DO 30 ITYPE=1,9
      IF(TYPE.EQ.TYPES(ITYPE)) GO TO 40
   30 CONTINUE
      IF(TYPE.EQ.QUIT) CALL SYSTEM
      IF(TYPE.NE.PPP) GO TO 31
      IF(IPP.GT.0) K=IPP
      ICK=5
      IF(IPP.LE.0) ICK=0
      IPP=0
      GO TO 15
   31 IF(IERR.EQ.0) WRITE(2,35)
   35 FORMAT('0THAT''S CLOSE, BUT THIS ISN''T HORSESHOES')
      IERR=IERR+1
      IF(IERR.LT.3) GO TO 15
      WRITE(2,37)
   37 FORMAT('1COLOR ME GONE'/1H1)
      CALL SYSTEM
   40 IERR=0
   50 GO TO(100,100,300,400,500,600,700,800,900),ITYPE
  100 IF(SET(6).LE.0.) GO TO 600
  110 IF(IC.EQ.0) WHICHS=ITYPE
      IF(IC.GT.0)WHICHS=IC
      IF(IPP.LE.0) GO TO 115
      V=VEE(WHICHS)
      J=IPP
      IPP=0
      GO TO 136
  115 IF(IS.GT.0) GO TO 130
      IS=10
      WRITE(2,120)WHICHS
  120 FORMAT('0ENTER V,J,LAMBDA AND MAXIT(NO OF ITER) FOR S',
     1I1,' (NAMELIST=&INS)')
      GO TO 135
  130 WRITE(2,133)
  133 FORMAT('0ENTER S PAR''S')
  135 CALL SETPFX('?',1)
      NAMELIST/INS/V,J,DOJ,LAMBDA,MAXIT,COMM
      READ(1,INS,ERR=135)
      CALL SETPFX(' ',1)
  136 VEE(WHICHS)=V
      JAY(WHICHS)=J
  137 CONTINUE
      V=VEE(WHICHS)
      J=JAY(WHICHS)
      PCON=FLOAT(J*(J+1)) - LAMBDA
      R=RMIN
C
C   POTENTIAL GENERATION
      DO 150 I=1,N
      GO TO (141,142,143),IPOT
C   MORSE
  141 RFACT=1.0-EXP(-DBETA*(R-DRE))
      U(I)=DDE*(RFACT*RFACT-1.0)
```

NOT REPRODUCIBLE

```
          IF(RCON .NE. 0.) U(I)=U(I)+RCON/(R*R)
          GO TO 145
C     NUNHAM
  142     RF=(R-DRE)/DRE
          U(I)=BWF*RF*RF
          SUMUU=0.
          DO 144 II=1,4
  144     SUMUU=SUMUU+U(II)*A(II)*RF**II
          U(I)=U(I)+SUMUU-DDE
          IF(RCON .NE. 0.) U(I)=U(I)+RCON/(R*R)
          GO TO 145
C     RKP
  143     CALL LAGTRP(RS,W,NW,R,ULAG,3,&145,&145)
          U(I)=ULAG*MUCON-DDE
          IF(RCON.NE.0)  U(I)=U(I)+RCON/(R*R)
  145     R=R+H
  150     CONTINUE
C     OBTAIN INITIAL ENERGY ESTIMATE
          CALL MAXENG(V,J,ENG)
          ENG=ENG*MUCON
          EZERO=ENG-DDE
          ESAVE=EZERO
          EPS=ABS(EPSCON*EZERO)
          EMAX(WHICHS)=EZERO/MUCON
          EPSCM=EPS/MUCON
          KNODES=0
          IF(ICK.LE.0) GO TO 290
          CALL SETPFX(' ',1)
          WRITE(2,250)(U(J),J=1,N,K)
  250     FORMAT(1H0,T10,'POTENTIAL FUNCTION'/
         1(1H ,1P5E14.6))
C     CALL SCHR TO OBTAIN EIGENFUNCTION
  290     CONVRG=1.0*SCHR(WHICHS)
          EMAR(WHICHS)=EZERO/MUCON
          IF(CONVRG.NE.0.) WRITE(2,291)EPSCM
C     CHECK FOR CONVERGENCE
  291     FORMAT(' SPECIFIED ERROR EPS=',1PE14.7,' NOT OBTAINED.')
          IF(KNODES.NE.V) WRITE(2,292)KNODES,V
C     CHECK FOR CORRECT NUMBER OF NODES
  292     FORMAT(' SOLUTION HAS ',I2,' NODES BUT V IS',I2,' ).E.',
         1' WRONG EIGENFUNCTION')
          SET(WHICHS)=10.
          IF(ITYPE.EQ.2) GO TO 530
          IF(DOJ.EQ.0) GO TO 193
          WHICHS=2
          ITYPE=2
          GO TO 137
  193     IF(IC) 530,15,530
  300     WRITE(2,305)
  305     FORMAT('CENTER M0,M1,M2, AND M3 AS FOLLOWS :' /
         1' &INM M0=   ,M1=    ...  &END'  )
          NAMELIST/INM/M0,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11
          CALL SETPFX('?',1)
          READ(1,INM)
C     CALCULATE MOMENT VALUES
          CALL SETPFX(' ',1)
          WRITE(2,306)M0,M1,M2,M3
  306     FORMAT('0MOMENT TERMS ARE:'/,T10,4F15.6/)
          R=(RMIN-DRE)/DRE
          HC=H/DRE
          DO 350 I=1,N
          M(I)=M0+(M1+(M2+(M3+(M4+(M5+(M6+(M7+(M8+(M9+(M10+M11*R)*R)*R)
         1*R)*R)*R)*R)*R)*R)*R)*R
          R=R+HC
```

NOT REPRODUCIBLE

```
  350  CONTINUE
       KK=ITYPE
       IF(IC.NE.0) KK=IC
       SET(KK)=10.
       IF(IC)530,15,530
  400  SET(ITYPE-1)=10.
       DO 450 I=1,N
  450  M(I)=1.0
       GO TO 15
  500  DO 505 IC=1,3
       IF(SET(IC).LT.0.) GO TO 510
  505  CONTINUE
       IC=0
       GO TO 530
  510  WRITE(2,511) TYPES(IC)
  511  FORMAT('0PLEASE SET ',A4)
       GO TO(100,100,300),IC
C    INTEGRATE PRODUCT S1*S2*M
  530  SUM=0.
       DO 535 I=1,N
       XLOG=ALOG(ABS(S1(I)))+ALOG(ABS(S2(I)))+ALOG(ABS(M(I)))
       P(I)=0.
       IF(XLOG.LT.-170.) GO TO 535
       P(I)=S1(I)*S2(I)*M(I)
       SUM=SUM+P(I)
       SU(I)=SUM
  535  CONTINUE
C    DETERMINE LINE POSITION
       PMOR=ABS(EMOR(1)-EMOR(2))
       PMAN=ABS(EMAN(1)-EMAN(2))
       AREA=(SUM-.5*(P(1)+P(N)))*H
       ASQ=AREA**2
       AA=3.1365E20*ASQ*PMAN**3
       NSUM=IPP
       IPP=IABS(IPP)
       IF(NSUM.GE.1)WRITE(2,536)(P(I),I=1,N,IPP)
  536  FORMAT('0PROD S1*S2*M'/(1H ,1P6E11.4))
       IF(NSUM.LE.-1)WRITE(4,537)(SU(I),I=1,N,IPP)
  537  FORMAT('1INDIVIDUAL AREA SUMMATION STEPS'/(1H ,1P6E11.3))
C    WRITE OUTPUT
       IF(ISTEP.GE.1) GO TO 545
       WRITE(2,542)COMM
       WRITE(2,540)PNAME(IPOT)
       WRITE(2,542)COMM
       WRITE(2,541)
  540  FORMAT('0 V1 V2 J1 J2  <S1 M S2>    <S1 M S2>**2  NU(',A4,
     1')  NU(TERM)'/,' ')
  541  FORMAT('0 V1 V2 J1 J2   <S1 M S2>          A',
     1'      LINE POSITION'/,19X,'ESU           SFC-1        CM-1')
  542  FORMAT('1  ',5A4)
  545  WRITE(2,543)VEE(1),VEE(2),JAY(1),JAY(2),AREA,ASQ,PMOR,PMAN
       WRITE(3,544)VEE(1),VEE(2),JAY(1),JAY(2),AREA,AA,PMAN
  543  FORMAT(' ',4I3,1P2E13.5,0P2F10.2)
  544  FORMAT(' ',4I3,1P2E13.5,0PF13.2)
       IF(JAY(1).EQ.0.OR.JAY(2).EQ.0) GO TO 2015
       IF(DOJ.EQ.0) GO TO 2015
       JAY(1)=JAY(1)-1
       JAY(2)=JAY(2)-1
       DOJ=DOJ-1
       ISTEP=ISTEP+1
       IF(ISTEP.GT.40) ISTEP=0
       WHICHS=1
       ITYPE=1
       GO TO 137
```

```
 2015  DDJ=0
       GO TO 15
C   SET UP POTENTIAL FUNCTION PARAMETERS
 600   WRITE(2,610)
 610   FORMAT('C3 POTENTIAL TYPES ARE ALLOWED :'/
      1' MORSE(1),DUNHAM(2) AND FALLON RKR(3)'
      2/' ENTER  A 1,2, OR 3 FOR THE TYPE DESIRED')
       SET(6)=10.
       CALL SETPFX('?',1)
       READ(1,615)IPOT
 615   FORMAT(I10)
       CALL SETPFX(' ',1)
       GO TO (620,630,640),IPOT
 620   WRITE(2,622)
 622   FORMAT('0FOR MORSE POTENTIAL ENTER ',
      1 'EITHER DE OR WEXE,'/' AND WE,BE AND '
      2'MUSUBA IN 1/CM'/' THE NAMELIST TO USE IS "MORS"')
       NAMELIST/MORS/DE,WEXE,WE,RE,BE,MUSUBA/
      1INPUT/NW,W,RS,MUSUBA/RIN/RMAX,RMIN,N,EPSCON
       DE=0.0
       WEXE=0.0
       CALL SETPFX('?',1)
       READ(1,MORS)
       CALL SETPFX(' ',1)
       CALL MORSE(DE,WE,WEXE,RE,BE,BETA,MUSUBA)
       GO TO 650
 630   WRITE(2,632)
 632   FORMAT('0 DUNHAM POTENTIAL WILL BE USED.')
       WE=4149.04
       BE=20.956
       WEXE=90.05
       RE=.9168E-8
       DE=WE*WE/(4.*WEXE)
       GO TO 650
 640   WRITE(2,642)
 642   FORMAT('0  RKR HF POTENTIAL WILL BE USED')
       IF(SET(7).GT.0.) GO TO 650
       CVRT=.529172
       DO 645 I=1,NW
       RS(I)=RS(I)/CVRT
 645   CONTINUE
       DE=47150.
       RE=.901E-8
       SET(7)=10.
 650   DRE=RE/.529172E-8
       MUCON=MUSUBA/60.2198
       DDE=DE*MUCON
       DWE=WE*MUCON
       DBETA=BETA*MUCON
       BWE=(WE*WE*MUCON)/(4.*BE)
       WRITE(2,652)DE,WEXE,RE,BETA
 652   FORMAT('0DE , WEXE , RE AND BETA IN 1/CM ARE:'/
      1 1H ,1P4E15.6)
       WRITE(2,655) DRE
C   SET UP RANGE AND INCREMENT FOR INTEGRATION
 655   FORMAT('0RE = ',F10.7,' , ENTER RMAX,RMIN,EPSCON AND'
      1' N USING NAMELIST "RIN"')
       CALL SETPFX('?',1)
       READ(1,RIN)
       CALL SETPFX(' ',1)
       H=(RMAX-RMIN)/FLOAT(N)
       IF(ITYPE-6)50,15,50
 700   CONTINUE
       CALL SETPFX(' ',1)
```

NOT REPRODUCIBLE

```
      WRITE(2,750) TYPES(1),(S1(I),I=1,N,K)
  750 FORMAT(1H0,20X,A4/(1P4E16.7))
      GO TO 15
  800 CONTINUE
      CALL SETPFX(' ',1)
      WRITE(2,750)TYPES(2),(S2(I),I=1,N,K)
      GO TO 15
  900 CONTINUE
      CALL SETPFX(' ',1)
      WRITE(2,750)TYPES(3),(M(I),I=1,N,K)
      GO TO 15
      END
C   SCHRODINGER EQUATION SOLUTION PROGRAM
      FUNCTION SCHR(WHICHS)
      REAL*8 Y,P,H,H2,HV,PM,DF,F,DOLD,DE,YOUT,Y1N,YM,E,EOLD
     1,GN,GI
      DATA PRNT/5./
      COMMON P,S1,S2,U,RMAX,RMIN,N,KNODES,EZERO,EPS,MAXIT
      DIMENSION P(2005),S1(2005),S2(2005),U(2005),Y(3)
      INTEGER WHAT,WHICHS
      PRNT=-10.
      IF(MAXIT.GT.0) GO TO 5
      MAXIT=-MAXIT
      PRNT=10.
C
    5 N1=N-1
      H=(RMAX-RMIN)/FLOAT(N)
      H2= H *H
      HV=H2/12.
      E=EZERO
      TEST=-1.
      DE=0.
      DO 171 IT=1,MAXIT
      P(N)=1.0E-30
      GN=U(N)-E
      GI=U(N1)-E
      IF(GI.GE.0.0) GO TO 10
      SCHR=-10.0
      RETURN
C   START INWARD INTEGRATION
   10 P(N1)=P(N)*DEXP(RMAX*DSQRT(GN)-(RMAX-H)*DSQRT(GI))
      Y(1)=(1.-HV*GN)*P(N)
      Y(2)=(1.-HV*GI)*P(N1)
      M=N-2
   46 Y(3)=Y(2)+((Y(2)-Y(1))+H2*GI*P(M+1))
      GI=U(M)-E
      DIV=1.-HV*GI
      IF(ABS(DIV).GT. 1.0E-30) GO TO 65
      M1=M+1
      PM=P(M1)
      DO 56 J=M1,N
   55 P(J)=P(J)/PM
      DO 60 I=1,3
   60 Y(I)=Y(I)/PM
      GI=U(M1)-E
      GO TO 46
   65 P(M)=Y(3)/DIV
      IF(DABS(P(M)).LE.DABS(P(M+1))) GO TO 90
      IF(M.LE.2) GO TO 90
      Y(1)=Y(2)
      Y(2)=Y(3)
      M=M-1
      GO TO 46
   90 PM=P(M)
```

NOT REPRODUCIBLE

NOT REPRODUCIBLE

```
      MSAVE=M
      YIN=Y(2)/PM
      DO 96 J=M,N
   96 P(J)=P(J)/PM
      P(1)=1.0E-20
C   START OUTWARD INTEGRATION
      Y(1)=0.
      GI=U(1)-E
      Y(2)=(1.-HV*GI)*P(1)
      DO 132 I=2,M
  110 Y(3)=Y(2)+((Y(2)-Y(1))+H2*GI*P(I-1))
      GI=U(I)-E
      DIV=1.-HV*GI
      IF(ABS(DIV).GT. 1.0E-30) GO TO 130
      I1=I-1
      PM=P(I1)
      DO 120 J=1,I1
  120 P(J)=P(J)/PM
      DO 125 J=1,3
  125 Y(J)=Y(J)/PM
      GI=U(I1)-E
      GO TO 110
  130 P(I)=Y(3)/DIV
      Y(1)=Y(2)
      Y(2)=Y(3)
  132 CONTINUE
      PM=P(M)
      F=1.5E30
      IF(PM.EQ.0) GO TO 148
      YOUT=Y(1)/PM
      YM=Y(3)/PM
      DO 140 J=1,M
  140 P(J)=P(J)/PM
      DF=0.
      DO 146 J=1,N
C   GENERATE ENERGY CORRECTION
  146 DF=DF-P(J)*P(J)
      F=(-YOUT-Y)N+2.*YM)/H2+U(M)-E
      DOLD=DE
  148 IF(F .LT. 1.0E30) GO TO 150
  149  F=1.0E30-1.
      DF=-F
      DE= DABS(.0001*F)
      GO TO 152
  150 DE=-F/DF
  152 EOLD=E
      E=E+DE
      TEMP1=DABS(DOLD)- DABS(DE)
      IF(TEMP1.GT.TEST) TEST=TEMP1
      IF(TEST.LT.0.)GO TO 171
C   CHECK FOR CONVERGENCE
      IF(DABS(E-EOLD).LE.EPS) GO TO 172
  171 IF(PRNT.GT.0.) WRITE(2,500) IT,DE,EOLD,E,F
  500 FORMAT(1H ,I5,1P4E15.6)
      SCHR=1.0
      GO TO 173
  172 SCHR=0.0
C   COUNT NODES
  173 KV=0
      NL=N-2
      DO 192 J=3,NL
      IF(P(J).LT.0.) GO TO 178
      IF(P(J-1)) 180,192,192
  178 IF(P(J-1)) 192,187,184
```

NOT REPRODUCIBLE

```
      180   IF(P(J+1)).192,182,182
      182   IF(P(J-2))190,192,192
      184   IF(P(J+1) .GE.0.)GO TO 192
            IF(P(J-2))192,190,190
      187   IF(P(J+1) .GE.0.) GO TO 192
            IF(P(J-2).LE.0.)  GO TO 192
      190   KV=KV+1
      192   CONTINUE
            SN=DSQRT(-H*DE)
            GO TO (200,300) , WHICHS
      200   DO 250 J=1,N
      250   S1(J)=P(J)/SN
            GO TO 400
      300   DO 350 J=1,N
      350   S2(J)=P(J)/SN
      400   EZERO=E
            KNOTES=KV
            RETURN
            END
C     SUBROUTINE TO GENERATE INITIAL ENERGY
            SUBROUTINE MANENG(V,J,E)
            INTEGER VV,V
            DIMENSION Y(6,6)
            DATA Y/0.,4138.73,-90.65,.932,-1.42E-2,-5.9E-4,20.9555,-.7958,
           11.132E-2,-3.11E-4,-5.8E-6,0.,-2.153E-3,6.23E-5,-2.06E-6,
           20.,0.,0.,1.69E-7,-6.5E-9,0.,0.,0.,0.,-1.25E-11,0.,0.,0.,0.
           3,0.,0.,0.,0.,0.,0.,0./
            VX=FLOAT(V)+.5
            JX=FLOAT(J*(J+1))
            E=0.
            VP=1./VX
            DO 350 VV=1,6
            VP=VP*VX
            E=E+VP*Y(VV,1)
            JP=1.
            IF(JX.LT..5) GO TO 300
            DO 250 JJ=2,6
            JP=JX*JP
      250   E=E+Y(VV,JJ)*VP*JP
      300   CONTINUE
            RETURN
            END
C     SUBROUTINE TO GENERATE MORSE DIMENSIONLESS PARAMETERS
            SUBROUTINE MORSE(DE,WE,WEXE,RE,BC,BETA,MUSUBA)
            REAL MUSUBA,MUCON
            MUCON=MUSUBA/60.2198
            W=WE*MUCON
            B=BE*MUCON
            IF(ABS(DE).GT.ABS(WEXE)) GO TO 20
            WX=WEXE*MUCON
            D=(W*W)/(4.*WX)
            D=D/MUCON
            GO TO 30
      20    D=ABS(DE*MUCON)
            WX=(W*W)/(4.*D)
            WEXE=WX/MUCON
      30    R=SQRT(1./B)
            RE=R*.52917 2E-8
            BT=SQRT(WX)
            BETA=BT/MUCON
            RETURN
            END
END OF FILE
```

REFERENCES

1. R. Herman and R. F. Wallis, "Influence of Vibration-Rotation Interaction on Line Intensities in Vibration-Rotation Bands of Diatomic Molecules," J. Chem. Phys., Vol. 23, 1955, p. 637.
2. R. E. Meredith, Matrix Elements for the v = 0⟶3, 2⟶3, and 3⟶4 Vibration-Rotation Bands of Diatomic Molecules," Report No. 4613-138-T, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, February 1967.
3. H. S. Heaps and G. Herzberg, "Intensity Distribution in the Rotation-Vibration Spectrum of OH Molecule," Z. Physik, Vol. 133, 1952, p. 48.
4. R. E. Meredith, Strengths and Widths in the First Overtone Band of Hydrogen Fluoride, Report No. 8416-27-T, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, August 1969.
5. R. J. Lovell and W. F. Herget, "Lorentz Parameters and Vibration-Rotation Interaction Constants for the Fundamental Band of HF," J. Opt. Soc. Am., Vol. 52, 1962, p. 1374.
6. G. Herzberg, Molecular Spectra and Molecular Structure I: Diatomic Molecules, D. VanNostrand, Inc., New York, 1950.
7. R. Rydberg, "Graphic Representation of Some Results in Band Spectroscopy," Z. Physik, Vol. 73, 1931, p. 376 and Vol. 80, 1933, p. 514.
8. A. L. G. Rees, "The Calculation of Potential-Energy Curves from Band Spectroscopic Data," Proc. Phys. Soc., Vol. 59, 1947, p. 998.
9. J. L. Dunham, "The Energy Levels of a Rotating Vibrator," Phys. Rev., Vol. 41, 1932, p. 721.
10. R. N. Zare and J. K. Cashion, "The IBM Share Program D2 NU SCHR 1072 for Solution of the Schrodinger Radial Equation, by J. W. Cooley: Necessary and Useful Modifications for Its Use on an IBM 7090," UCRL Report No. 10881, University of California Radiation Laboratory, 1963.
11. J. K. Cashion, "Testing of Diatomic Potential Energy Functions by Numerical Methods," J. Chem. Phys., Vol. 39, 1963, p. 1872.
12. J. W. Cooley, "An Improved Eigenvalue Corrector Formula for Solving the Schrodinger Equation for Central Fields," Math. Computation, Vol. 15, 1961, p. 363.
13. E. A. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, 1959.