The MORBID Method

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1 Introduction

The present communication is concerned with the problem of calculating the
rotation-vibration energies and the absorption intensities of a triatomic molecule
from the effective nuclear potential energy function and the dipole moment sur-
faces within the Born-Oppenheimer approximation (Born & Oppenheimer 1927).
There are at least two astrophysical applications of such calculations:

- Detailed spectra of triatomic molecules can be computed under the condi-
  tions prevailing in stellar atmospheres and compared with observed spectra.
- Such spectra can also be used for constructing a wavenumber-dependent ab-
  sorption coefficient which can be employed for opacity calculations as out-
  lined, for example, by Jørgensen & Jensen (1993).

In the Born-Oppenheimer approximation (Born & Oppenheimer 1927), the
rovibronic energies of a molecule are calculated in two steps:

- In the first step, the nuclei are held fixed in space, and the Schrödinger
  problem for the electrons (which interact with the "clamped" nuclei and
  with each other through Coulomb forces) is solved for many different nuclear
  geometries. The energy eigenvalue obtained in this calculation, taken as a
  function of the nuclear coordinates (which we denote as $\mathbf{R}_n$ here), is the
  Born-Oppenheimer potential energy function $V(\mathbf{R}_n)$.
- The second step is the solution of the Schrödinger equation for the nuclear
  motion,

$$\left[\widehat{T}_n + V(\mathbf{R}_n)\right]\psi_n(\mathbf{R}_n) = E_{ne}\psi_n(\mathbf{R}_n) \tag{1}$$

  where $\widehat{T}_n$ is the operator representing the kinetic energy of the nuclei, $\psi_n(\mathbf{R}_n)$
  is a nuclear wavefunction, and E_{ne} is the corresponding energy eigenvalue.

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One may think of the motion of the nuclei as a superposition of translation (uniform motion of all nuclei along straight lines through space), vibration (motion of the nuclei relative to each other), and rotation. It can be shown that the nuclear kinetic energy operator $\widehat{T}_n$ can be separated into the sum of two commuting operators

$$\widehat{T}_n = \widehat{T}_{\text{Trans}} + \widehat{T}_{\text{Rot}-\text{Vib}}, \tag{2}$$

where $\widehat{T}_{\text{Trans}}$ describes the kinetic energy resulting from translation and $\widehat{T}_{\text{Rot}-\text{Vib}}$ that resulting from rotation and vibration. In theoretical studies aimed at describing "spectroscopic" phenomena (i.e., the interaction between molecules and radiation) for isolated molecules in a field-free space we can ignore the effects of translation since radiation will not induce transitions between translational states. We are then left with the Schrödinger equation for rotation and vibration

$$\left[\widehat{T}_{\text{Rot}-\text{Vib}} + V(\mathbf{R}_{\text{Vib}})\right] \psi_{\text{Rot}-\text{Vib}}(\mathbf{R}_{\text{Rot}}, \mathbf{R}_{\text{Vib}}) = E_{\text{Rot}-\text{Vib}}\psi_{\text{Rot}-\text{Vib}}(\mathbf{R}_{\text{Rot}}, \mathbf{R}_{\text{Vib}}). \tag{3}$$

In Eq. (3), we have indicated that the rotation-vibration wavefunction $\psi_{\text{Rot}-\text{Vib}}$ depends on rotational coordinates $\mathbf{R}_{\text{Rot}}$ and vibrational coordinates $\mathbf{R}_{\text{Vib}}$, whereas the potential energy function V depends on the vibrational coordinates only.

We discuss here the solution of Eq. (3). In theoretical spectroscopy, the traditional approach to obtaining the rotation-vibration energies $E_{\text{Rot}-\text{Vib}}$ and the corresponding eigenfunctions $\psi_{\text{Rot}-\text{Vib}}$ involves perturbation theory: The molecular vibration is modelled by a set of independent harmonic oscillators, and the molecular rotation is modelled as that of a rigid molecule. The deviation between the real molecule and this idealized model is treated as a perturbation.

In recent years it has become apparent that in many cases, the perturbation treatment of molecular rotation and vibration leads to considerable inaccuracies in the calculated energies, and a number of more accurate methods for solving Eq. (3) have been developed for small (mostly triatomic) molecules. In the present communication we shall describe one such method for triatomic molecules, the MORBID (Morse Oscillator Rigid Bender Internal Dynamics) approach (Jensen 1988a, 1988b, 1992). The computer programs developed on the basis of the MORBID model can be used for three different types of calculations:

- If the nuclear potential energy function $V(\mathbf{R}_n)$ for one isolated electronic state is known, the rotation-vibration energies belonging to this electronic state can be calculated.
- The parameters in an analytical representation for $V(\mathbf{R}_n)$ (see below) can be refined in a least squares fitting to experimentally observed rotation-vibration energy spacings.
- If $V(\mathbf{R}_n)$ and the dipole moment components are known as functions of the nuclear coordinates, absorption spectra (i.e., transition wavenumbers and intensities) can be calculated.

We give examples of such calculations below.

2 The MORBID Approach

We give here a very sketchy outline of the ideas behind the MORBID approach. The reader is referred to Jensen (1988a, 1988b, 1992) for details.

2.1 Coordinates

In order to describe a quantum mechanical system such as a triatomic molecule, we must initially choose a set of coordinates defining its instantaneous configuration. In the MORBID approach, we follow the work of Hougen et al. (1970) in that we base the coordinate definitions on a socalled reference configuration (Fig. 1) which follows the rotation and the bending motion. The reference configuration is chosen as having fixed internuclear distances r_{j2}^e [the equilibrium distance between the "outer" nucleus $j = 1$ or 3 (Fig. 1) and the center nucleus 2], but with a variable bond angle α. The coordinate $\rho = \pi - \alpha$ is chosen to describe the large amplitude motion, and the stretching motions are described as displacements from the reference geometry through the coordinates

$$\Delta r_{j2} = r_{j2} - r_{j2}^e, \tag{4}$$

$j = 1$ or 3, defined as the displacement of the instantaneous internuclear distance r_{j2} from its equilibrium value r_{j2}^e. We attach a molecule fixed axis system xyz to the reference configuration (Fig. 1) and describe the rotation of the molecule through usual Euler angles θ, ϕ, and χ (see, for example, Papoušek & Aliev (1982)) which give the instantaneous orientation of the xyz axis system relative to a laboratory fixed axis system XYZ.

2.2 The potential energy operator

We choose the potential energy function for a triatomic molecule to be given by the analytical function

$$V(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = V_0(\bar{\rho}) + \sum_j F_j(\bar{\rho})y_j + \sum_{j \le k} F_{jk}(\bar{\rho})y_j y_k$$

$$+ \sum_{j \le k \le m} F_{jkm}(\bar{\rho})y_j y_k y_m + \sum_{j \le k \le m \le n} F_{jkmn}(\bar{\rho})y_j y_k y_m y_n, \tag{5}$$

where all of the indices j, k, m, and n assume the values 1 or 3. In Eq. (5), $\bar{\rho}$ is the supplement of the instantaneous value of the bond angle (which is almost, but not quite, equal to the vibrational coordinate ρ discussed above), and

$$y_j = 1 - \exp(-a_j \Delta r_{j2}), \tag{6}$$

where the Δr_{j2} are defined in Eq. (4) and the a_j are molecular parameters. The $F_{jkm...}$ expansion coefficients of Eq. (5) are functions of $\bar{\rho}$. The function $V_0(\bar{\rho})$ is the pure bending potential energy function, i.e. the potential energy for the molecule bending with its bond lengths fixed at their equilibrium values.
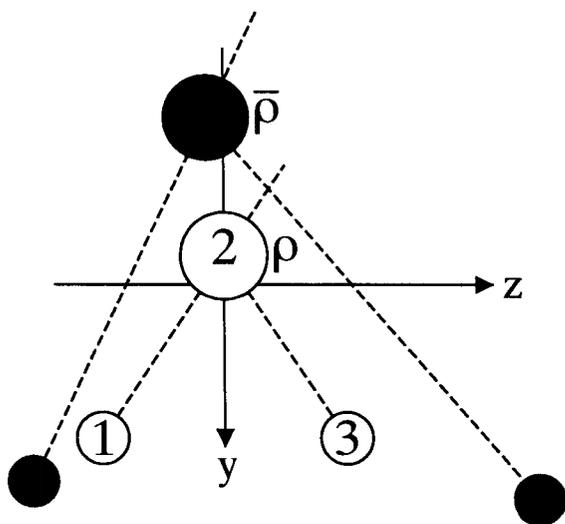
Fig. 1. The numbering of the nuclei and the molecule fixed coordinate system used in the MORBID approach. The molecule fixed x axis is perpendicular to the plane of the molecule. The open circles are the positions of the nuclei in the reference configuration (which has the bond angle supplement ρ) and the filled circles are the instantaneous positions of the nuclei (with bond angle supplement $\bar{\rho}$).

The $\bar{\rho}$-dependent functions entering into Eq. (5) are defined as general cosine expansions:

$$F_j(\bar{\rho}) = \sum_{i=1}^{4} f_j^{(i)}(\cos \rho_e - \cos \bar{\rho})^i,$$

$$F_{jk\ldots}(\bar{\rho}) = f_{jk\ldots}^{(0)} + \sum_{i=1}^{N} f_{jk\ldots}^{(i)}(\cos \rho_e - \cos \bar{\rho})^i \tag{7}$$

where ρ_e is the equilibrium value of $\bar{\rho}$ and the $f_{jk\ldots}^{(i)}$ are expansion coefficients. The function $F_{jk}(\bar{\rho})$ has $N = 3$, $F_{jkl}(\bar{\rho})$ has $N = 2$, and $F_{jklm}(\bar{\rho})$ has $N = 1$. Symmetry relations exist between the potential energy parameters for the symmetrical ABA molecule to ensure that V is totally symmetric under the interchange of Δr_{12} and Δr_{32}. For $V_0(\bar{\rho})$, we use two different parameterizations,

$$V_0(\bar{\rho}) = \sum_{i=2}^{8} f_0^{(i)}(\cos \rho_e - \cos \bar{\rho})^i, \tag{8}$$

or

$$V_0(\bar{\rho}) = \sum_{i=1}^{8} f_0^{(i)}(1 - \cos \bar{\rho})^i. \tag{9}$$

The parameterization given by Eq. (8) has ρ_e as an independent parameter and is appropriate for *bent* molecules, i.e. molecules with $\rho_e \neq 0$. Equation (9) has $f_0^{(1)}$ as an independent parameter, whereas ρ_e is determined as a function of the $f_0^{(i)}$ quantities. This parameterization is appropriate for both linear and bent molecules.

For a potential energy function with a single minimum, the analytical expression given by Eqs. (5-9) has a physically reasonable asymptotic behaviour at all coordinate boundaries: at $\bar{\rho} = 0$ and $\bar{\rho} = \pi$ it has zero slope for all values of r_{12} and r_{32}, at large bond length values it approaches a constant for any value of $\bar{\rho}$, and at short bond lengths it approaches a very large (although not infinite) value.

2.3 The kinetic energy operator

Using the rules of quantum mechanics, we can derive a kinetic energy operator $\hat{T}_{\text{MORBID}}$ expressed in terms of the coordinates given in Sect. 2.1. This operator is obtained as

$$\hat{T}_{\text{MORBID}} = \frac{1}{2} \sum_{\delta,\gamma=x,y,z,\rho} (\hat{J}_\delta - \hat{p}_\delta)\mu_{\delta\gamma}(\Delta r_{12}, \Delta r_{32}, \rho)(\hat{J}_\gamma - \hat{p}_\gamma)$$

$$+ \frac{1}{2} \sum_{j,k=1,3} \hat{P}_j G_{jk}^{(r)}(\Delta r_{12}, \Delta r_{32}, \rho)\hat{P}_k + U_1(\Delta r_{12}, \Delta r_{32}, \rho) + U_0(\rho), \quad (10)$$

where $\hat{J}_\delta$, $\delta = x, y, z$, are the components of the total angular momentum along the molecule fixed axes, $\hat{J}_\rho = -i\hbar\partial/\partial\rho$, $\mu_{\delta\gamma}$ ($\delta, \gamma = x, y, z, \rho$) are the elements of the 4×4 "inverse inertial" matrix μ defined by Eqs. (45-50) of Jensen (1988a), $\hat{P}_j = -i\hbar\partial/\partial\Delta r_{j2}$ is the momentum conjugate to Δr_{j2}, the vibrational angular momentum $\hat{p}_\delta$ is given by

$$\hat{p}_\delta = \frac{1}{2} \sum_{j,k=1,3} \left\{ \hat{P}_j G_{jk}^{(r)} \chi_k^{(\delta)} + \chi_k^{(\delta)} G_{jk}^{(r)} \hat{P}_j \right\}, \quad (11)$$

the $\chi_k^{(\delta)}$ being Coriolis coupling coefficients, and the $G_{jk}^{(r)}$ matrix elements are defined by Eq. (40) of Jensen (1988a). The U_1 and U_0 functions are pseudopotential terms defined in Eqs. (42-44) of Jensen (1988a). The dependence of U_0 on the stretching coordinates Δr_{12} and Δr_{32} has been neglected; this possibly explains why sometimes splittings due to Fermi resonances are calculated to be too small by the MORBID program [see Bunker et al. (1990) and Barclay et al. (1993)].

The functions $\mu_{\delta\gamma}$, $G_{jk}^{(r)}$, and $\chi_k^{(\delta)}$ entering into Eq. (10) all depend on the coordinates Δr_{12}, Δr_{32}, and ρ, and we expand them as polynomials in y_1 and y_3 with ρ-dependent coefficients, e.g.

$$\mu = \mu_0(\rho) + \sum_j \mu_j(\rho)y_j + \sum_{j \leq k} \mu_{jk}(\rho)y_j y_k$$

$$+ \sum_{j \leq k \leq m} \mu_{jkm}(\rho)y_j y_k y_m + \sum_{j \leq k \leq m \leq n} \mu_{jkmn}(\rho)y_j y_k y_m y_n \quad (12)$$

where $\mu_{jk\ldots}(\rho)$ is a 4×4 matrix with elements $\mu_{\delta\gamma}^{(jk\ldots)}(\rho)$, δ, $\gamma = x$, y, z, ρ. The expansion of the μ-tensor elements are truncated after the quartic terms, the expansions of the $\chi_k^{(\delta)}$ functions are truncated after the cubic terms, and the expansions of the $G_{jk}^{(r)}$ matrix elements are truncated after the quadratic terms. In this way, we obtain $\widehat{T}_{\text{MORBID}}$ as an expansion to fourth order in the vibrational operators y_j and $\widehat{P}_k$.

2.4 The calculation of the rotation-vibration energies

The MORBID Hamiltonian is now given as

$$\widehat{H}_{\text{MORBID}} = \widehat{T}_{\text{MORBID}} + V(\Delta r_{12}, \Delta r_{32}, \rho) \tag{13}$$

where $\widehat{T}_{\text{MORBID}}$ is given by Eq. (10) (with the coordinate-dependent functions expressed as the series expansions described above) and the potential function V from Eq. (5) has been transformed so that instead of depending on Δr_{12}, Δr_{32}, and the instantaneous value of the bond angle supplement $\bar{\rho}$ [see Sect. 2.2], it now depends on Δr_{12}, Δr_{32}, and the coordinate ρ. The transformation is carried out using basic geometrical identities as shown in Eqs. (34-36) of Jensen (1988a).

We obtain the solutions of the eigenvalue problem

$$\widehat{H}_{\text{MORBID}}\ \psi_{\text{MORBID}}(\Delta r_{12}, \Delta r_{32}, \rho, \theta, \phi, \chi)$$
$$= E_{\text{MORBID}}\ \psi_{\text{MORBID}}(\Delta r_{12}, \Delta r_{32}, \rho, \theta, \phi, \chi) \tag{14}$$

by "taking the molecule apart". That is, we consider three simplified molecules, each of which only carries out part of the molecular motion.

Stretching. We initially consider a molecule which carries out stretching of its bond lengths r_{j2} with the bond angle fixed at the equilibrium value α_e and the rotation frozen. This molecule has the Hamiltonian

$$\widehat{H}_{\text{Stretch}} = \frac{1}{2}\left[\frac{1}{m_1} + \frac{1}{m_2}\right]\widehat{P}_1^2 + \frac{1}{2}\left[\frac{1}{m_3} + \frac{1}{m_2}\right]\widehat{P}_3^2 - \frac{1}{m_2}\cos\rho_e\,\widehat{P}_1\widehat{P}_3$$
$$+ \sum_{j \leq k} f_{jk}^{(0)} y_j y_k + \sum_{j \leq k \leq m} f_{jkm}^{(0)} y_j y_k y_m + \sum_{j \leq k \leq m \leq n} f_{jkmn}^{(0)} y_j y_k y_m y_n \tag{15}$$

[see Eq. (58) of Jensen (1988a)], where m_j is the mass of nucleus j. We obtain the eigenfunctions $|N_{\text{Vib}}\varGamma_{\text{Sym}}\rangle$ of this Hamiltonian [and the corresponding eigenvalues, which are our zero order stretching energies] by setting up the matrix of $\widehat{H}_{\text{Stretch}}$ in a basis of symmetrized Morse oscillator functions as described in Sect. V of Jensen (1988a). The eigenfunctions are labeled by the index N_{vib} which characterizes the zeroth order stretching state, and by $\varGamma_{\text{Sym}}$ which is the irreducible representation spanned by the function $|N_{\text{vib}}\varGamma_{\text{Sym}}\rangle$ in the appropriate molecular symmetry group.

Bending and K-Type Rotation. We then consider a molecule which carries out bending motion and rotation around the molecule-fixed z axis (Fig. 1) with its bond lengths fixed at the equilibrium values r_{12}^e and r_{32}^e. The molecule fixed z-axis becomes the molecular axis when the molecule is in a linear configuration. It is necessary to consider these two types of motion together since, for a triatomic molecule with a linear equilibrium configuration, the rotation around the z-axis is only made possible through the bending motion. This simplified molecule has the Hamiltonian

$$
\widehat{H}_{\text{Bend}} = \frac{1}{2} \widehat{J}_\rho \mu_{\rho\rho}^{(0)}(\rho) \widehat{J}_\rho + \frac{1}{2} \mu_{zz}^{(0)}(\rho) \widehat{J}_z^2
$$
$$
+ \frac{1}{2} \hbar^2 \mu_{\rho\rho}^{(0)}(\rho) \; g(\rho) + \frac{1}{2} (\mu^{(0)})^{-1/4} [\widehat{J}_\rho, \mu_{\rho\rho}^{(0)}][\widehat{J}_\rho, (\mu^{(0)})^{1/4}] + V_0(\rho), \quad (16)
$$

[see Eq. (63) of Jensen (1988a)] where $\mu^{(0)}$ is the determinant of the matrix $\boldsymbol{\mu}_0$ from Eq. (12), and the function $g(\rho)$ is given by Eq. (43) of Jensen (1988a). We obtain the eigenfunctions $|v_2, K\rangle$ for this Hamiltonian through Numerov-Cooley numerical integration (Cooley 1961) as described in Sect. V of Jensen (1988a). The index v_2 is the bending quantum number for a bent triatomic molecule, and K is the rotational quantum number describing the rotation around the z-axis.

End-over-end Rotation. Finally, we consider a drastically simplified molecule which carries out rotation around the molecule fixed x- and y-axes. We assume this molecule to be a rigid symmetric top, so that its rotational eigenfunctions are the symmetrized symmetric top eigenfunctions $|J, K, M, \tau\rangle$ defined in Eq. (7.1) of Jensen (1983).

The Complete Molecule. We use the products $|N_{\text{vib}} \Gamma_{\text{Sym}}\rangle |v_2, K\rangle |J, K, M, \tau\rangle$ as basis functions for constructing a matrix representation of the rovibrational Hamiltonian $\widehat{H}_{\text{MORBID}}$ for the "complete" molecule. We may label the eigenfunctions ψ_{MORBID} of this Hamiltonian through an index s together with the good quantum numbers J, M, and Γ_{rv}, where $M\hbar$ is the projection of the total angular momentum on the space-fixed Z-axis and Γ_{rv} is the symmetry of the wavefunction, and we approximate such a function as

$$
\psi_{\text{MORBID}} = |s; J, M, \Gamma_{rv}\rangle
$$
$$
= \sum_{N_{\text{vib}}, \Gamma_{\text{Sym}}, v_2, K} c_{N_{\text{vib}}, \Gamma_{\text{Sym}}, v_2, K}^{(s; J, M, \Gamma_{rv})} |N_{\text{vib}} \Gamma_{\text{Sym}}\rangle |v_2, K\rangle |J, K, M, \tau\rangle. \quad (17)
$$

By diagonalizing the matrix representation of the Hamiltonian, we can determine its eigenvalues (which, in the approximation adopted here, are the rotation-vibration energies) and the expansion coefficients $c_{N_{\text{vib}}, \Gamma_{\text{Sym}}, v_2, K}^{(s; J, M, \Gamma_{rv})}$ defining the rotation-vibration wavefunction in Eq. (17).

2.5 Intensity calculations

With the rotation-vibration wavefunctions given by Eq. (17) we can calculate the intensities of absorption transitions between rotation-vibration states. If we consider molecules in thermal equilibrium at an absolute temperature T, the integrated absorption coefficient for a transition from an initial state $|s_i; J_i, M_i, \Gamma_{rv(i)}\rangle$ to a final state $|s_f; J_f, M_f, \Gamma_{rv(f)}\rangle$ is given by (Smith et al. 1985)

$$I(f \leftarrow i) = \frac{8\pi^3 N_A g_{ns}\omega_{if} \exp(-E_i/kT)[1 - \exp(-hc\omega_{if}/kT)]}{3hcQ} S(f \leftarrow i) \quad (18)$$

where N_A is Avogadro's number, g_{ns} is the nuclear spin statistical weight, ω_{if} is the wavenumber of the transition (in cm^{-1}), E_i is the energy of the initial state, k is the Boltzmann constant, h is Planck's constant, c is the vacuum velocity of light and the partition function Q is given by

$$Q = \sum_w g_w \exp(-E_w/kT). \quad (19)$$

In Eq. (19), E_w is the energy and g_w the total degeneracy of the state w and the summation extends over all such states of the molecule. The line strength $S(f \leftarrow i)$ of an electric dipole transition is defined as

$$S(f \leftarrow i) = \sum_{A=X,Y,Z} \sum_{M_i,M_f} \left| \langle s_f; J_f, M_f, \Gamma_{rv(f)} | \mu_A | s_i; J_i, M_i, \Gamma_{rv(i)} \rangle \right|^2 \quad (20)$$

where μ_A is the component of the electronically averaged molecular dipole moment operator along the A axis ($A = X$, Y, or Z) of the space fixed coordinate system and M_i and M_f are the rotational M quantum numbers (quantizing the Z component of the total angular momentum) of the initial and final states, respectively.

As described by Jensen (1988c), the MORBID program can calculate the linestrengths given by Eq. (20) on the basis of the wavefunctions from Eq. (17) and the electronically averaged dipole moment surfaces of the molecule. The dipole moment functions are chosen as follows: A pq axis system is defined for the triatomic molecule. This axis system has its origin at the nuclear center of mass and the p and q axes are in the plane defined by the three nuclei. For an unsymmetrical ABC molecule, the p axis is parallel to the bond between nucleus 2 and nucleus 3 and points so that the p coordinate of nucleus 1 is negative. The q axis is perpendicular to the p axis and points so that the q coordinate of nucleus 1 is positive. For a symmetical ABA molecule, the q axis is the bisector of the angle $\angle(\text{ABA})$ and points so that the two A nuclei have positive q-coordinates. The p axis is perpendicular to the q axis and points so that the p coordinate of nucleus 3 is positive. The dipole moment component along the p axis, $\bar{\mu}^{(p)}$, is expanded as:

$$\bar{\mu}^{(p)}(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = \mu_0^{(p)}(\bar{\rho}) + \sum_j \mu_j^{(p)}(\bar{\rho})\Delta r_{j2}$$

$$+ \sum_{j \leq k} \mu_{jk}^{(p)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} + \sum_{j \leq k \leq m} \mu_{jkm}^{(p)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} \Delta r_{m2}$$

$$+ \sum_{j \leq k \leq m \leq n} \mu_{jkmn}^{(p)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} \Delta r_{m2} \Delta r_{n2}, \tag{21}$$

where all of the indices j, k, m, and n assume the values 1 or 3 and

$$\mu_{jk\ldots}^{(p)}(\bar{\rho}) = \sum_{i=0}^{N} p_{jk\ldots}^{(i)} (\cos \rho_e - \cos \bar{\rho})^i. \tag{22}$$

The function $\mu_0^{(p)}(\bar{\rho})$ has $N = 8$, $\mu_j^{(p)}(\bar{\rho})$ has $N = 4$, $\mu_{jk}^{(p)}(\bar{\rho})$ has $N = 3$, $\mu_{jkm}^{(p)}(\bar{\rho})$ has $N = 2$, and $\mu_{jkmn}^{(p)}(\bar{\rho})$ has $N = 1$.

The dipole moment component along the q axis, $\bar{\mu}^{(q)}$, is represented by

$$\bar{\mu}^{(q)}(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = \sin \bar{\rho} \left[\mu_0^{(q)}(\bar{\rho}) + \sum_j \mu_j^{(q)}(\bar{\rho}) \Delta r_{j2} \right.$$

$$+ \sum_{j \leq k} \mu_{jk}^{(q)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} + \sum_{j \leq k \leq m} \mu_{jkm}^{(q)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} \Delta r_{m2}$$

$$\left. + \sum_{j \leq k \leq m \leq n} \mu_{jkmn}^{(q)}(\bar{\rho}) \Delta r_{j2} \Delta r_{k2} \Delta r_{m2} \Delta r_{n2} \right]. \tag{23}$$

Again, all of the indices j, k, m, and n assume the values 1 or 3. The equations for the $\mu_{jkm\ldots}^{(q)}(\bar{\rho})$ functions are obtained when p is replaced by q in Eq. (22).

The values of the parameters $p_{jk\ldots}^{(i)}$ and $q_{jk\ldots}^{(i)}$ in Eqs. (21-23) are obtained by fitting the analytical expressions through ab initio dipole moment values. As explained by Jensen (1988c)

- The dipole moment components along the molecule fixed y and z axes, μ_y and μ_z, can be obtained by rotating the components $\bar{\mu}^{(p)}$ and $\bar{\mu}^{(q)}$.
- The functions μ_y and μ_z can be transformed into polynomials in the quantities $y_k = 1 - \exp(-a_k \Delta r_{k2})$ [with expansion coefficients depending on the bending coordinate ρ].
- The matrix elements of these expansions between vibrational basis functions can be straightforwardly calculated using Morse oscillator matrix elements from Špirko et al. (1985).
- On the basis of the vibrational matrix elements of μ_y and μ_z and the expansion coefficients $c_{N_{\text{vib}}, \Gamma_{\text{Sym}}, v_2, K}^{(s; J, M, \Gamma_{rv})}$ from Eq. (17), the line strength $S(f \leftarrow i)$ for an individual rotation-vibration transition can be obtained from Eq. (55) of Jensen (1988c).

When the linestrengths $S(f \leftarrow i)$ have been obtained, the integrated absorption coeffients $I(f \leftarrow i)$ can be calculated from Eq. (18) if the absorbing molecules are in thermal equilibrium. For non-equilibrium situations the calculation of $I(f \leftarrow i)$ requires detailed knowledge about the population distribution

of the molecules under study. In order to allow direct comparison with experimental results it might be necessary to compute peak absorption coefficients for the rotation-vibration transitions. Such calculations require further knowledge about the line shape function (i.e., about the broadening effects present in the experiment). An example of a calculation of this type is given by Jensen et al. (1992).

3 Applications

We give here a brief survey of results from MORBID calculations.

3.1 H₂O

Calculations from ab initio data. Two calculations of the rotation-vibration energies of the water molecule have been carried out (Jensen 1988b,1988d) on the basis of ab initio potential energy surfaces from Kraemer et al. (1982) and Bartlett et al. (1987), respectively.

Fitted potential energy surfaces. The parameters of Eqs. (5-9) have been optimized (Jensen 1989a) through a least squares fitting to an extensive set of rotation-vibration energy spacings for $H_2{}^{16}O$ and its isotopic species. These input data consisted of 550 experimental energy separations involving rotation-vibration energy levels with $J \leq 2$ in 103 vibrational states [with energies up to $19\,000$ cm^{-1} above the (0,0,0) state] belonging to the six isotopic molecules $H_2{}^{16}O$, $D_2{}^{16}O$, $HD{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, and $T_2{}^{16}O$. In the fitting 19 parameters were varied, and the standard deviation was 0.63 cm^{-1}. In a careful comparison between four potential energy surfaces for water available in the literature (Jensen 1989a; Carter & Handy 1987; Halonen & Carrington 1988; Kauppi & Halonen 1990) Fernley et al. (1991) found the MORBID potential (Jensen 1989a) to be the most accurate surface currently available for the water molecule. This potential has also been used for calculations of water energies by Wattson & Rothman (1992) and by Choi & Light (1992). On the basis of the MORBID potential energy surface and dipole moment surfaces calculated ab initio, Jørgensen and Jensen (1993) have recently carried out an extensive calculation of the vibrational transition moments for water, which they intend to use as input for an accurate calculation of the absorption coefficient as a function of wavenumber. A new refined potential for H₂O based on experimental data involving $J \leq 10$ is presently being fitted with the MORBID program (Jensen & Tyuterev 1993).

3.2 CH₂

Calculations from ab initio data. Ab initio calculations of the rotation-vibration energies in the vibrational ground state $\tilde{X}{}^3B_1$ of the methylene radical CH₂ have been carried out by Jensen (1988a) (who used a potential energy surface calculated by McLean et al. (1987)) and by Comeau et al. (1989), who also did calculations for the first excited electronic state $(\tilde{a}{}^1A_1)$.

Fitted potential energy surfaces. Jensen & Bunker (1988) have fitted the potential energy surfaces for the $\widetilde{X}^3B_1$ and $\widetilde{a}^1A_1$ electronic states of CH_2. For the $\widetilde{X}^3B_1$ state, they used all extant rotation-vibration data as input for the fitting, whereas only the $J = 0$ data for the $\widetilde{a}^1A_1$ state were fitted. On the basis of the fitted potential energy surfaces, the stretching fundamental energies of $\widetilde{X}^3B_1$ $^{12}CH_2$ were predicted at $E(\nu_1) = 2992$ cm^{-1} and $E(\nu_3) = 3213$ cm^{-1}. By combining the results of the MORBID fittings with experimental data for the $\widetilde{X}$ and $\widetilde{a}$ states Jensen & Bunker (1988) obtained the energy splitting between the vibrational ground states of these two electronic states as $T_0\left(\widetilde{a}^1A_1\right) = 3147$ cm^{-1} (8.998 kcal/mol) and the splitting between the equilibrium energies of the two states as $T_e\left(\widetilde{a}^1A_1\right) = 3223$ cm^{-1} (9.215 kcal/mol) for $^{12}CH_2$.

3.3 C_3

Calculations from ab initio data. The rotation-vibration energy spectrum of C_3 in the electronic ground state have been calculated by Jensen & Kraemer (1988a) on the basis of an ab initio potential energy surface by Kraemer et al. (1984). Recently, more extensive ab initio calculations have been carried out by Jensen et al. (1992). These authors also considered the intensities of the allowed ν_2 and ν_3 fundamental bands of $^{12}C_3$ and showed that their theoretical transition moments were in keeping with recent experimental observations (Schmuttenmaer et al. 1990).

Fitted potential energy surfaces. Jensen (1989b) fitted a very limited set of rovibrational data for $^{12}C_3$ and obtained a potential energy function with a small barrier to linearity (16.5 cm^{-1}). This agreed well with the ab initio results by Kraemer et al. (1984) and apparently supported suggestions by Matsumura et al. (1988) who argued on experimental grounds that C_3 might be slightly bent. A recent fit to a more extended data set by Jensen et al. (1992), however, yields a potential energy surface with a linear equilibrium geometry, in agreement with the ab initio calculation by these authors.

3.4 H_2Se

Jensen & Kozin (1993) have fitted a potential energy surface for the electronic ground state of hydrogen selenide H_2Se. On the basis of this potential energy function, the rovibrational energy structure in the vibrational ground state (Jensen & Kozin 1993) and in the fundamental vibrational states (Kozin & Jensen 1993) has been calculated. In all the vibrational states studied, it was found that four-fold energy clusters (i.e., four-member groups of nearly degenerate energies) form at high rotational excitation. This effect has been experimentally verified for the vibrational ground state of $H_2{}^{80}Se$ (Kozin et al. 1992a, 1992b, 1993).

3.5 Other molecules

Other molecules for which MORBID calculations have been carried out include NH_2^+ (Jensen et al. 1987; Barclay et al. 1993), HOC^+ (Jensen & Kraemer 1988a), CCN^+ and CNC^+ (Jensen & Kraemer 1988b), LiOH (Bunker et al. 1989), NH_2 (Jensen et al. 1990), H_2F^+ (Bunker et al. 1990), HNC^+ (Kraemer et al. 1992), Si_2C (Barone et al. 1992), HO_2 (Bunker et al. 1992), and HNSi (Chong et al. 1993).

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