dem Energieunterschied der Niveaus ab, ähnlich wie die Größe der induzierten Emission von der Strahlungsdichte, ihrer Frequenzverteilung und der Anregungsenergie des Überganges abhängt. Genauso wie für die technische Anwendung der induzierten Emission eine spezielle Strahlungsverteilung (es wird nicht die Planck-Verteilung sein) günstig ist, so wird auch bei den induzierten Stoßprozessen eine spezielle Elektronenverteilung (es wird nicht die Fermi-Verteilung sein) vorteilhaft sein.

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The Dipole Moment Function of H^{79}Br Molecule

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The radial Schrödinger wave equation with Morse potential function is solved for H^{79}Br molecule. The resulting vibration-rotation eigenfunctions are then used to compute the matrix elements of $(r-r_e)^n$. These are combined with the experimental values of the electric dipole matrix elements to calculate the dipole moment coefficients, M_1 and M_2.

Introduction

In the case of the vibration-rotation transitions occurring in a given electronic state of a heteronuclear diatomic molecule, the electric dipole matrix element $\mathbf{M}_{v'',J''}^{v',J'}$ is given by

$$\mathbf{M}_{v'',J''}^{v',J'} = \int \Psi_{v',J'}^{*}(r)\, M(r)\, \Psi_{v'',J''}(r)\, r^2\, \mathrm{d}r \qquad (1)$$

where $\Psi_{v',J'}(r)$ and $\Psi_{v'',J''}(r)$ are the radial eigenfunctions of the upper and lower vibration-rotation states respectively. $M(r)$ is the molecular electric dipole moment function which is conveniently expanded about the equilibrium internuclear distance, r_e, and is written as

$$M(r) = M_0 + M_1(r-r_e) + M_2(r-r_e)^2 + \dots \qquad (2)$$

where M_0 is the permanent dipole moment and M_1, M_2, etc. are the dipole moment coefficients. Substituting Eq. (2) in Eq. (1) we get

$$\mathbf{M}_{v'',J''}^{v',J'} = M_1 \int \Psi_{v'J',}^{*}(r)\,(r-r_e)\,\Psi_{v'',J''}(r)\, r^2\, \mathrm{d}r + M_2 \int \Psi_{v',J'}^{*}(r)\,(r-r_e)^2\, \Psi_{v'',J''}\, r^2\, \mathrm{d}r + \dots \qquad (3)$$

The coefficients M_1, M_2, etc. can be determined if the values of the dipole matrix elements for the various vibration-rotation transitions and the eigenfunctions of the states involved are known. The former can be obtained from the experimentally measured spectral line strengths whereas the latter depend on the type of the potential function $V(r)$ used to represent the diatomic molecule.

In the present work we have chosen the Morse potential function[1] which adequately represents the true potential of the diatomic molecule. It is given by

$$V(r) = D_e[1 - \exp\{-\beta(r-r_e)\}]^2 \qquad (4)$$

where D_e is the dissociation energy of the molecule expressed in cm^{-1} units and β is a constant to be determined.

The radial Schrödinger wave equation for a diatomic molecule can be written as

$$\frac{\mathrm{d}^2\Psi_{v,J}(r)}{\mathrm{d}r^2} + \left\{ \frac{8\pi^2\mu}{h^2}[E_{v,J} - V(r)] - \frac{J(J+1)}{r^2} \right\} \Psi_{v,J}(r) = 0 \qquad (5)$$

where μ is the reduced mass of the molecule and $E_{v,J}$ is the energy of the vibration-rotation state charaterized by the vibrational quantum number v and the rotational quantum number J. When the Morse potential [Eq. (4)] is substituted for $V(r)$, the above equation can be solved rigorously for the case $J=0$ to yield the pure vibrational eigenfunctios, Ψ_v. Using these eigenfunctions HEAPS and HERZBERG[2] evaluated the two integrals in Eq. (3)

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for the case $J = 0$ in terms of the usual molecular constants. RAO[3] used their expressions and the experimentally determined vibrational matrix elements $M_{v''}^{v'}$ to determine the dipole moment coefficients M_1 and M_2 for the hydrogen bromide molecule, $H^{79}Br$. Thus, in his calculations, RAO[3] ignored the influence of rotation on the dipole moment function.

In this paper we have extended Rao's work on $H^{79}Br$ molecule to include this rotational contribution. To calculate the eigenfunctions of the various vibration-rotation states of the HBr molecule, the radial Schrödinger wave equation using the Morse potential function was solved numerically with the aid of IBM 360-40 computer. These eigenfunctions were then used to calculate the two integrals in Equation (3). Finally the dipole moment coefficients were evaluated by using these integrals and the experimental values of the matrix elements of the $1-0$ and $2-0$ vibration-rotation bands of the $H^{79}Br$ molecule.

Calculations

All the molecular constants for the HBr molecule used in the present calculations were obtained from the data of RANK et al.[4].

A) Morse Parameters, D_e and β

In order to find an initial estimate of D_e and β to be used in the calculations, the vibrational term values $G(v)$ were first calculated from the molecular constants for the vibrational states with $v = 0$, 1, 2, and 3. These term values are related to Morse parameters through the expression

$$G(v) = \beta \sqrt{\frac{D_e\, h}{2\,\pi^2\, c\,\mu}}\,(v+\tfrac{1}{2}) - \frac{h\,\beta^2}{8\,\pi^2\, c\,\mu}\,(v+\tfrac{1}{2})^2. \tag{6}$$

The values of D_e and β were then obtained by using a least squares fit to the above equation.

B) Eigenvalues and Eigenfunctions

To solve the radial Schrödinger wave equation numerically, we used a computer program similar to that used by LOUCKS[5]. This program uses the Runge-Kutta and Milne techniques. In the program, a grid of 388 points was chosen for the internuclear distance r within a range of $1 \times 10^{-8}\, a_0 \leqq r \leqq 7\, a_0$ where a_0 is the Bohr unit of length.

The eigenvalues E were obtainend in the following way. A value of $E_{v,J}$ was arbitrarily chosen and the radial wave equation was solved outward from $r = 10^{-8}\, a_0$ and inward from $r = 7\, a_0$ upto the equilibrium internuclear distance, r_e. At r_e, the logarithmic derivatives for these two solutions were evaluated and compared. The initial estimate of $E_{v,J}$ was then changed and the comparison of the logarithmic derivatives was repeated. This process was continued until the two were equal at r_e. The value of $E_{v,J}$ satisfying this condition was taken as the appropriate eigenvalue.

As a check on the accuracy of our computer program, we ran it with the Morse parameters for HCl molecule used by CASHION[6]. The vibrational eigenvalues obtained from our program were then compared with those found by Cashion who used the computer techniques developed by Cooley and Numerov to solve the radial wave equation. These are shown in Table 1. The excellent agreement between the two sets of the eigenvalues gives us the confidence in the methods we have used.

Table 1. The vibrational eigenvalues calculated using Cashion's program and our program for HCl molecule.

	$E_{v,0}$ in Rydbergs		
v	Cashion's	Ours	Difference
0	0.013491005	0.013490990	1.5×10^{-8}
1	0.039651547	0.039651519	2.8×10^{-8}
2	0.064716808	0.064716808	0
3	0.088686793	0.088686793	0
4	0.111561503	0.111561503	0
5	0.133340931	0.133340940	0.9×10^{-8}

From the eigenvalues calculated using the initial Morse parameters D_e and β, the vibration-rotation transition frequencies were found. These were then compared to the experimentally measured transition frequencies. The parameters were then systematically varied until a good agreement between the calculated and experimental transition frequencies were found.

The eigenfunctions corresponding to these eigenvalues were then obtained. The sign convention chosen was such that the eigenfunctions were all made positive for the increasing values of the internuclear distance, r. The eigenfunctions were then normalized and checked for the orthogonality condition and the values of the orthogonality integrals were found to be less than 10^{-6}.

Results and Discussion

The values of the Morse parameters D_e and β were found to be 0.355937 Rydbergs and 0.861549 a_0^{-1} respectively. Using these values we have evaluated the eigenvalues and the eigenfunctions of the first eleven states in the $1-0$ and $2-0$ vibration-rotation bands. For the $1-0$ band, the sign of the values of the first integral in Eq. (3) turned out to be negative. This made us choose a negative sign for the value of $\boldsymbol{M}^{1,J'}_{0,J''}$ in order to keep the coefficient M_1 to be positive. To be consistent with the rotational distribution of the dipole matrix elements of both the $1-0$ and $2-0$ bands, we had to choose a negative sign for $\boldsymbol{M}^{1,J'}_{0,J''}$ and a positive sign for $\boldsymbol{M}^{2,J'}_{0,J''}$. The values of the dipole matrix elements, obtained from the papers published by RAO and his students [7, 8], were then combined with the computed values of the integrals in Eq. (3) to calculate the values of the dipole moment coefficients, M_1 and M_2. They are found to be $M_1 = 0.315$ Debye/Å and $M_2 = 0.575$ Debye/Å^2. The above calculation uses the least squares method and is confined to quadratic fit only. We have tried and rejected the cubic fit since it gave a larger standard error. Taking $M_0 = 0.788$ Debye for the permanent dipole moment as listed by WESSON [9], the dipole moment function of the $H^{79}Br$ molecule can be expressed by the following equation:

$$M(r) = 0.788 + 0.315\,(r - r_e) + 0.575\,(r - r_e)^2 . \quad (7)$$

The values obtained by RAO [3], who ignored the rotational contribution in his calculations, are $M_1 = 0.316$ Debye/Å and $M_2 = 0.518$ Debye/Å^2. These are very close to the values presented in this paper.

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