NOTIZEN

The Dipole Moment Function of HF Molecule Using Morse Potential

Y. K. Chan and B. S. Rao

Department of Physics, University of North Dakota

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The radial Schrödinger wave equation with Morse potential function is solved for HF 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.

The electric dipole matrix element $\mathcal{M}_{v'',J''}^{v',J'}$ of a heteronuclear diatomic molecules is given by

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

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

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

In the above expression, 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

$$\begin{aligned}\mathcal{M}_{v'',J''}^{v',J'} &= M_1 \int \psi_{v',J'}^{*}(r)\,(r-r_e)\,\psi_{v'',J''}(r)\, r^2\, \mathrm{d}r \\ &+ M_2 \int \psi_{v',J'}^{*}(r)\,(r-r_e)^2\,\psi_{v'',J''}(r)\, r^2\, \mathrm{d}r\,. \qquad (3)\end{aligned}$$

The coefficients M_1 and M_2 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 dipole matrix elements $\mathcal{M}_{v'',J''}^{v',J'}$ can be derived from the experimentally measured spectral line strengths. The eigenfunctions of the states can be calculated by solving the radial Schrödinger wave equation with a proper potential function for the diatomic molecule.

To calculate the dipole moment coefficients M_1 and M_2 for the hydrogen fluoride molecule, we have chosen the Morse potential function [1] 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 characterized by the vibrational quantum number v and the rotational quantum number J.

The Morse potential function [Eq. (4)] is substituted in the radial Schrödinger wave equation [Eq. (5)] and the eigenfunctions corresponding to the various states are then calculated with the aid of computers. These eigenfunctions are used to obtain the two integrals in Equation (3). Finally, the dipole moment coefficients are 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 HF molecule. All the calculations performed in this work are quite similar to those we have done on HBr molecule and the details of the calculations were published earlier in this journal [2].

The values of the Morse parameters, D_e and β, and the internuclear distance r_e are found to be $D_e = 0.4891265$ Rydberg, $\beta = 1.208173\, a_0{}^{-1}$ and $r_e = 1.7322534\, a_0$ where a_0 is the Bohr unit of length. These were obtained by comparing the calculated transition frequencies with the experimentally measured ones by Webb and Rao [3]. Using these values of the Morse parameters, we have evaluated 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 value of the first integral in Eq. (3) turned out to be negative. This made us choose negative sign for the value of $\mathcal{M}_{0,J''}^{1,J'}$ in order to keep the coefficient M_1 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 negative sign for $\mathcal{M}_{0,J''}^{1,J'}$ and positive sign for $\mathcal{M}_{0,J''}^{2,J'}$. The values of the dipole matrix elements were experimentally measured by Lovell and Herget [4] for the 1–0 band and by Meredith [5, 6] for the 2–0 band. These are 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 $M_1 = 1.259$ Debye/Å and $M_2 = 3.507$ Debye/Å^2. The above cal-

Reprint requests to Dr. B. Sesh Rao, Department of Physics, University of North Dakota, *Grand Forks, N. D. 58201*, U.S.A.

culation 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 $M_0 = 1.91$ Debye for the permanent dipole moment as listed by Wesson[7], the dipole moment function of the HF molecule can be expressed by the following equation:

$$M(r) = 1.91 + 1.259\,(r - r_e) + 3.507\,(r - r_e)^2.$$

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