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Determination of ω_e, $\omega_e x_e$, B_e, and α_e using potential energy functions for heteronuclear diatomic molecules via spreadsheet program

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Abstract

In order to represent the potential energy function over the whole range of *R*, many potential energy functions have been proposed. In the present paper, we employ many potential energy functions, to use Numerov method for solving the nuclear Schrödinger equation for the IF molecule, as an example of a heteronuclear diatomic molecules. Then we determine the spectroscopic constants ω_e, $\omega_e x_e$, B_e, and α_e of the IF molecule from vibrational and vibration-rotation levels obtained from solution of the nuclear Schrödinger equation. Finally, by comparison of obtained values with the experimental ones, their accuracy rate is determined as well as their deviation percentages from experimental values.

Keywords: Spectroscopic constants; Potential energy functions; Heteronuclear diatomic molecules

1. Introduction

The molecular Schrödinger equation is extremely complicated to solve. The exact solution of this equation is a formidable task due to the fact that the electronic and nuclear degrees of freedom are scrambled in the related molecular Hamiltonian [1-5]. Based on the fact that nuclei are much heavier than electrons, the Born-Oppenheimer approximation is a very efficient method to treat the electronic and nuclear motions separately [6]. The electronic Schrödinger equation and nuclear Schrödinger equation are as follows:

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}, \tag{1}$$

$$(\hat{T}_N + U)\psi_N = E\psi_N, \tag{2}$$

where U is the electronic energy including internuclear repulsion which acts as the potential energy for the nuclear Schrödinger equation. For diatomic molecules, the potential energy U depends only on internuclear distance R. So this subject is a central-force problem [7-9]. As we know, the nuclear-motion wave function is

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$$\psi_N = Y_J^M(\theta_N \phi_N)P(R). \tag{3}$$

where the Y_J^M functions are the spherical harmonic functions with quantum number J and M, and $P(R)$ is the radial function.

So, the Schrödinger equation can be written in the form

$$\frac{-\hbar^2}{2\mu}F''(R) + \left[U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2}\right]F(R) = E_{\text{int}}F(R). \tag{4}$$

The latter equation looks like a one-dimensional Schrödinger equation with the effective potential energy $U(R) + J(J+1)\hbar^2 / 2\mu R^2$.

At first, our goal in the present paper is to solve the nuclear Schrödinger equation for heteronuclear diatomic molecules to obtain the vibration-rotation eigenvalues and eigenfunctions.

In the perturbative method, we may improve the approximation by taking further terms in the expansion of U. Note that, for large R, this expansion is not convergent. To represent the potential energy function over the whole range of R, many potential energy functions such as Morse, Rydberg, and so on, have been proposed [10-17]. These functions contain parameters (usually three) that are evaluated from experimental quantities for the molecular electronic state of interest [18].

In this paper, the nuclear Schrödinger equation for the IF molecule as a heteronuclear diatomic molecules will be solved by the Numerov method. The potential functions of Morse [19], Rydberg [20], Varshni(II) [21], Varshni(III) [21], Varshni(VI) [21], Poschl-Teller [22], Hulburt-Hirschfelder [23], Frost-Musulin [24], Linnet [25], Lippincott [26], and Rosen-Morse [27] are used to calculate the vibrational and vibration-rotation eigenvalues and eigenfunctions. The accuracy of these potential functions are estimated by comparing the available experimental values with the numerical results which we will obtain. Thereafter we will obtain the spectroscopic constants ω_e, $\omega_e x_e$, B_e, and α_e from computed vibrational and vibration-rotation energy levels.

2. Results and Discussion

2.1. Numerical solution of the vibrational Schrödinger equation of heteronuclear diatomic molecules

Since we are dealing with small quantities, to solve the Schrödinger equation by numerical methods, we should reformulate the equation using dimensionless variables. We seek to find a dimensionless reduced energy E_r and a dimensionless reduced x coordinate x_r which are defined as

$$x_r = \frac{x}{B}, \qquad E_r = \frac{E}{A}, \tag{5}$$

where the constant A has dimensions of energy, and B is a constant with dimensions of length. Now, for instance, we consider the Schrödinger equation with the Varshni(III) potential function. Substituting the Varshni(III) potential function into (4) with $J = 0$, the Schrödinger equation becomes

$$\frac{-\hbar^2}{2\mu}\psi''(x) + D_e\left[1 - \frac{r_e}{r}e^{-\beta(r^2 - r_e^2)}\right]^2 \psi = E\psi, \tag{6}$$

where $x = r - r_e$. Equation (6) contains the three constants μ, β, and $\hbar$. Thus, by using the constants, we can make the quantities of the equation dimensionless:

$$\left[\beta\right] = \mathrm{L}^{-2}, \qquad \left[\hbar\right] = \mathrm{ML}^{2}\mathrm{T}^{-1}, \qquad \left[\mu\right] = \mathrm{M}, \tag{7}$$

therefore

$$A = \mu^{-1}\beta\ \hbar^{2}. \tag{8}$$

let $B = \mu^{a}\beta^{b}\hbar^{c}$. Therefore

$$B = \beta^{-\frac{1}{2}}. \tag{9}$$

Since $\left|\psi(x)\right|^{2} dx$ is the probability which is dimensionless, the $\psi(x)$ must have the dimensions of length$^{-1/2}$. We now rewrite the Schrödinger equation with Varshni(III) potential function in terms of the reduced variables $D_{e,r}$, x_r, ψ_r, and E_r.

In view of (5), we have $dx_r/dx = B^{-1}$. Substituting (5), (8) and (9) into (6), we obtain

$$\frac{-\hbar^2}{2\mu}(\beta^{-1/2})^{-5/2}\frac{d^2\psi_r}{dx_r^2} + D_{e,r}(\mu^{-1}\beta\ \hbar^2)\left[1 - \frac{r_{e,r}\beta^{-1/2}}{(x_r + r_{e,r})\beta^{-1/2}} e^{-\beta(((x_r + r_{e,r})^2 - r_{e,r}^2)(\beta^{-1}))}\right]^2 \psi_r(\beta^{-1/2})^{-1/2}$$
$$= E_r(\mu^{-1}\beta\ \hbar^2)\psi_r(\beta^{-1/2})^{-1/2}. \tag{10}$$

Dividing by $B^{-1/2}$ and simplifying (10), we have

$$\frac{-\hbar^2}{2\mu}\beta\ \frac{d^2\psi_r}{dx_r^2} + D_{e,r}(\mu^{-1}\beta\ \hbar^2)\left[1 - \frac{r_{e,r}}{(x_r + r_{e,r})} e^{-(x_r^2 + 2x_r r_{e,r})}\right]^2 \psi_r = E_r(\mu^{-1}\beta\ \hbar^2)\psi_r. \tag{11}$$

Therefore,

$$\frac{d^2\psi_r}{dx_r^2} = \left[2D_{e,r}\left[1 - \frac{r_{e,r}}{(x_r + r_{e,r})} e^{-(x_r^2 + 2x_r r_{e,r})}\right]^2 - 2E_r\right]\psi_r. \tag{12}$$

Since

$$\psi'' = G\psi, \tag{13}$$

we have $\psi_r'' = G_r\psi_r$ and hence

$$G_r = 2D_{e,r}\left[1 - \frac{r_{e,r}}{(x_r + r_{e,r})} e^{-(x_r^2 + 2x_r r_{e,r})}\right]^2 - 2E_r. \tag{14}$$

Now, we are in the position to be able to solve the Schrödinger equation with Varshni(III) potential function via the Numerov method. In addition to finding the dimensionless expression G_r, we need to find relations between parameters that we need.

In order to find the relations between these parameters, we use the following three necessary conditions [16, 21, 28]:

$$U(r_e) - U(\infty) = -D_e, \tag{15}$$

$$\left(\frac{dU}{dr}\right)_{r=r_e} = 0, \tag{16}$$

$$\left(\frac{d^2U}{dr^2}\right)_{r=r_e} = k_e. \tag{17}$$

then, letting $\Delta = k_e r_e^2 / 2D_e$, we have

$$\beta = \frac{\Delta^{1/2} - 1}{2r_e^2}. \tag{18}$$

In a similar fashion, we can obtain relations between the parameters and the dimensionless expression G_r. Table 1 exhibits all potential functions together with their parameters and the dimensionless expression G_r. In the table, we make use of the symbols $\Delta = k_e r_e^2 / 2D_e$, $G = 8\omega_e x_e / B_e$, and $F = \alpha_e \omega_e / 6B_e^2$, where r_e, k_e, D_e, ω_e, $\omega_e x_e$, B_e, and α_e stand for the equilibrium bond length, force constant, dissociation energy, vibrational frequency, anharmonicity constant, equilibrium rotational constant, and the vibration-rotation coupling constant, respectively.

2.1.1. Determining s_r, $x_{r,0}$, *and* $x_{r,\max}$

To utilize the recursion relation [2]

$$\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + \frac{5}{6} G_n \psi_n s^2 + \frac{1}{12} G_{n-1} \psi_{n-1} s^2}{1 - G_{n+1} s^2 / 12}, \tag{19}$$

as well as the experession G_r, we need to determine the intial and final values of x_r and the distance s_r between the adjacent points. There are different methods to determine the intial and final values of x_r. First, we need to locate the boundaries between the classically allowed and forbidden regions. The boundaries consist of points at which $E_r = V_r$. Table 2 demonstrates A, $x_{r,0}$, $x_{r,\max}$, the spectroscopic numerical values, and the dimensionless expression G_r for the IF molecule with various potential energy functions.

Table 1
Potentials, relations between parameters, and the dimensionless expression G_r.

Potential	Potential function	Relations between parameters	The dimensionless expression G_r
Morse	$D_e\left[1-e^{-ax}\right]^2$	$a=\left(\frac{k_e}{2D_e}\right)^{1/2}$	$2D_{e,r}\left[1-e^{-x_r}\right]^2-2E_r$
Rydberg	$D_e\left[1-(1+dx)e^{-dx}\right]$	$d=\left(\frac{k_e}{D_e}\right)^{1/2}$	$2D_{e,r}\left[1-(1+x_r)e^{-x_r}\right]-2E_r$
Varshni (II)	$D_e\left[1-\frac{r_e}{r}e^{-a(r-r_e)}\right]^2$	$a=\frac{\Delta^{1/2}-1}{r_e}$	$2D_{e,r}\left[1-\frac{r_{e,r}}{x_r+r_{e,r}}e^{-x_r}\right]^2-2E_r$
Varshni (III)	$D_e\left[1-\frac{r_e}{r}e^{-\beta(r^2-r_e^2)}\right]^2$	$\beta=\frac{\Delta^{1/2}-1}{2r_e^2}$	$2D_{e,r}\left[1-\frac{r_{e,r}}{x_r+r_{e,r}}e^{-(x_r^2+2x_r r_{e,r})}\right]^2-2E_r$
Varshni (VI)	$D_e\left[1-\frac{r}{r_e}e^{-a(r-r_e)}\right]^2$	$a=\frac{\Delta^{1/2}+1}{r_e}$	$2D_{e,r}\left[1-\frac{x_r+r_{e,r}}{r_{e,r}}e^{-x_r}\right]^2-2E_r$
Poschl-Teller	$D_e+M\ \mathrm{cosech}^2\left(\frac{ar}{2}\right)-N\ \mathrm{sech}^2\left(\frac{ar}{2}\right)$	$\begin{cases} a=\left(\frac{k_e}{2D_e}\right)^{1/2} \\ N=\frac{D_e}{(1-y^2)^2} \\ M=N\,y^4 \\ y=\tanh\left(\frac{ar_e}{2}\right)\end{cases}$	$2\left[D_{e,r}+M_r\mathrm{cosech}^2\left(\frac{x_r+r_{e,r}}{2}\right)-N_r\mathrm{sech}^2\left(\frac{x_r+r_{e,r}}{2}\right)\right]-2E_r$
Hulburt-Hirschfelder	$D_e\left[1+e^{-2ax}-2e^{-ax}+ca^3x^3e^{-2ax}+ca^4x^4be^{-2ax}\right]$	$\begin{cases} a=\left(\frac{k_e}{2D_e}\right)^{1/2} \\ b=2-\frac{1}{c}\left\{\frac{7}{12}-\frac{1}{a^2r_e^2}\left[\frac{5}{4}+\frac{5F}{2}+\frac{5F^2}{4}+\frac{G}{12}\right]\right\} \\ c=1-\left(\frac{1}{ar_e}\right)(1+F)\end{cases}$	$2D_{e,r}\left[(1-e^{-x_r})^2+cx_r^3e^{-2x_r}(1-bx_r)\right]-2E_r$
Linnet	$D_e+\frac{a}{r^3}-be^{-nr}$	$\begin{cases} \Delta=\frac{3nr_e(nr_e-4)}{2nr_e-6} \\ a=\frac{nD_er_e^4}{3-nr_e} \\ b=\frac{3D_ee^{nr_e}}{3-nr_e}\end{cases}$	$2\left[D_{e,r}+\frac{a_r}{(x_r+r_{e,r})^3}-b_re^{-(x_r+r_{e,r})}-E_r\right]$
Rosen-Morse	$D_e+A\tanh\left(\frac{r}{d}\right)-C\mathrm{sech}^2\left(\frac{r}{d}\right)$	$\begin{cases} A=-2c\tanh\left(\frac{r_e}{d}\right) \\ c=\frac{D_e}{\left[1-\tanh\left(\frac{r_e}{d}\right)\right]^2}\end{cases}$	$2\left[D_{e,r}+A_r\tanh\left(x_r+r_{e,r}\right)-C_r\mathrm{sech}^2\left(x_r+r_{e,r}\right)-E_r\right]$

Table 1 continued

Potentials, relations between parameters, and the dimensionless expression G_r.

Potential	Potential function	Relations between parameters	The dimensionless expression G_r
Lippincott	$D_e\left[1-e^{\frac{-n(r-r_e)^2}{2r}}\right]$	$n=\frac{2\Delta}{r_e}$	$2D_{e,r}\left[1-e^{\frac{-x_r^2}{2(x_r+r_{e,r})}}\right]-2E_r$
Frost-Musulin	$D_e+e^{-ar}\left[\frac{c}{r}-b\right]$	$\begin{cases} a=\frac{\sqrt{1+2\Delta}-1}{r_e} \\ b=e^{ar_e}D_e(1+ar_e) \\ c=aD_e e^{ar_e}r_e^2 \end{cases}$	$2\left[D_{e,r}+e^{-(x_r+r_{e,r})}\left(\frac{c_r}{x_r+r_{e,r}}-b_r\right)-E_r\right]$

Table 2

A, $x_{r,0}$, $x_{r,\max}$, the spectroscopic numerical values, and the numerical dimensionless expression G_r for the IF molecule with various potential energy functions.

Potential	A	$x_{r,0}$	$x_{r,\max}$	Spectroscopic numerical values	The numerical dimensionless expression G_r
Morse	$a^2\hbar^2\mu^{-1}=6.1770$	-0.5	0.8	$a=1.740271\times10^8$	$2\times4879.9403\left[1-e^{-x_r}\right]^2-2E_r$
Rydberg	$d^2\hbar^2\mu^{-1}=12.3540$	-0.8	1.02	$d=2.461115\times10^8$	$2\times2439.9701\left[1-(1+x_r)e^{-x_r}\right]-2E_r$
Varshni (II)	$a^2\hbar^2\mu^{-1}=3.0190$	-0.29	0.4	$a=1.216645\times10^8$	$2\times9984.5615\left[1-\frac{2.3236}{x_r+2.3236}e^{-x_r}\right]^2-2E_r$
Varshni (III)	$\beta\hbar^2\mu^{-1}=0.6497$	-0.19	0.21	$\beta=3.185336\times10^{15}$	$2\times46397.29\left[1-\frac{1.0778}{x_r+1.0778}e^{-(x_r^2+2x_r\times1.0778)}\right]^2-2E_r$
Varshni (VI)	$a^2\hbar^2\mu^{-1}=10.4534$	-0.74	0.86	$a=2.263897\times10^8$	$2\times2883.5968\left[1-\frac{x_r+4.3236}{4.3236}e^{-x_r}\right]^2-2E_r$
Poschl-Teller	$a^2\hbar^2\mu^{-1}=6.1770$	-0.5	0.7	$\begin{cases} a=1.740271\times10^8 \\ N_r=270728.48 \\ M_r=202913.4736 \\ y=0.93045256 \end{cases}$	$2\left[4879.9403+202913.47\,\mathrm{cosech}^2\left(\frac{x_r+3.3236}{2}\right)-270728.48\,\mathrm{sech}^2\left(\frac{x_r+3.3236}{2}\right)\right]-2E_r$
Hulburt-Hirschfelder	$a^2\hbar^2\mu^{-1}=6.1770$	-0.52	0.7	$\begin{cases} a=1.740271\times10^8 \\ b=-0.348194552 \\ c=-0.033809103 \end{cases}$	$2\times4879.9\left[(1-e^{-x_r})^2-0.0338x_r^3e^{-2x_r}(1+0.3481x_r)\right]-2E_r$
Frost-Musulin	$a^2\hbar^2\mu^{-1}=8.0979$	-0.6	0.8	$\begin{cases} a=1.992576\times10^8 \\ b_r=804309.7531 \\ c_r=2424094.608 \end{cases}$	$2\left[3722.3714+e^{-(x_r+3.8058)}\left(\frac{2424094.6}{x_r+3.8058}-804309.7\right)-E_r\right]$

Table 2 continued

A, $x_{r,0}$, $x_{r,\max}$, the spectroscopic numerical values, and the numerical dimensionless expression G_r for the IF molecule with various potential energy functions

Potential	A	$x_{r,0}$	$x_{r,\max}$	Spectroscopic numerical values	The numerical dimensionless expression G_r
Linnet	$n^2\hbar^2\mu^{-1} = 3.4653$	-0.35	0.45	$\begin{cases} n=1.30347\times10^{8} \\ a_r=653791.9266 \\ b_r=615697.6035 \\ \Delta=11.04565649 \end{cases}$	$2\left[8698.6383+\dfrac{653791.9}{(x_r+2.4892)^{3}}-615697.6e^{-(x_r+2.4892)}-E_r\right]$
Rosen-Morse	$d^{-2}\hbar^2\mu^{-1} = 1.6458$	-0.25	0.35	$\begin{cases} d=1.113229\times10^{-8} \\ A_r=-8738943.401 \\ C_r=4661670.421 \end{cases}$	$2\left[8757258.744-8738943.4\tanh\left(x_r+1.7155\right)-4661670.4\operatorname{sech}^2\left(x_r+1.7155\right)-E_r\right]$
Lippincott	$n^2\hbar^2\mu^{-1} = 272.9158$	-3.5	4.5	$n=11.567585\times10^{8}$	$110.4494\left[1-e^{\frac{-x_r^2}{2(x_r+22.0909)}}\right]-2E_r$

2.1.2. Using spreadsheet program to obtain vibrational eigenvalues and eigenfunctions

Now that our input data G_r, s_r, $x_{r,0}$, and $x_{r,\max}$ are obtained, we can employ (19) by some software to draw the wave function and obtain the energy levels. Here we have used Excel spreadsheet program, which has the following benefits: 1) Having a friendly environment for programming, 2) Having a high power for numerical calculations, and 3) Having a high ability for sketching the wave functions.

Now, we examine the correctness of the operation as well as the initial guess for $E_{vib,r}$. By choosing the columns containing x_r and $nPsi_r$, we plot the wave function ψ_r against x_r. If the sketched function has the well-behaved conditions of a wave function and its value at $Psi_{r,\max}$ is close to zero, then the guess for $E_{vib,r}$ is satisfactory. But if the value of $Psi_{r,\max}$ is not close the zero we have to change the value of $E_{vib,r}$. To find a better value for $E_{vib,r}$ we proceed as follows. We first put zero for $E_{vib,r}$ in the cell B3 and then by using the solver option we ask the program to find the amount of energy such that $Psi_{r,\max}$ is as close to zero as possible. The solver option in Tools menu is one of the most useful features of Excel.

Since the cell F3 shows zero (Nodes = 0), we obtain the correct value of the first level of energy. To find the second level of energy we slightly increase the first level of energy. Again, by using solver option, we find a second level of energy. We must mention that the amount of increase must not be so high that the number of nodes reaches 2 or so low that the solver option can not find the next level of energy (a so-called “error”). We repeat the method for finding the next levels of energy. The number of nodes shows the kind of the state to which the energy belongs.

As a final control of the correct values of the energy levels, we have to check them against the plotted wave functions (see Appendix (B)). Finally the program multiplies the energy values $E_{vib,r}$ into the constant A to evaluate the energy values in terms of cm^{-1} (See Appendix (A), cell K3). In the same way, one can calculate the wave function and vibrational energy of the IF molecule with potential energy functions. In Table 3, the six lower level of vibrational energy levels of the IF molecule are obtained in terms of cm^{-1}, where one can also find their deviation percentages from the analytical calculations of the existing molecular constants [29] (in the table manual values are obtained from relation $\varepsilon_v = \omega_e(v+1/2) - \omega_e x_e (v+1/2)^2 + \ldots$).

Table 3
Six lower level of vibrational energy levels of the IF molecule in terms of cm^{-1} and deviation percentages from the analytical calculations of the existing molecular constants.

Potential	E_0	E_1	E_2	E_3	E_4	E_5	% error
Morse	304.3436	908.3837	1506.205	2097.783	2683.093	3262.116	0.005553
Rydberg	304.3891	908.9551	1507.834	2101.011	2688.469	3270.194	0.136874
Varshni(II)	304.2991	907.6058	1504.009	2093.526	2676.199	3252.248	-0.16252
Varshni(III)	304.4331	909.4955	1509.255	2103.54	2692.186	3275.037	0.232856
Varshni(VI)	304.3633	909.0096	1508.038	2101.426	2689.151	3271.192	0.15136
Poschl-Teller	304.3511	908.4116	1506.292	2097.992	2683.509	3262.843	0.015406
Lippincott	303.9794	909.3626	1509.86	2105.443	2696.082	3281.752	0.285899
Hulburt-Hirschfelder	304.3812	908.3633	1506.076	2097.5	2682.62	3261.419	-0.00294
Frost-Musulin	304.3616	908.4998	1506.54	2098.466	2684.266	3263.928	0.034345
Linnet	304.5278	909.8416	1510.265	2105.797	2696.438	3282.198	0.33651
Rosen-Morse	304.344	908.5784	1506.784	2098.932	2684.998	3264.957	0.051033
Manual value	304.34	908.34	1506.1	2097.62	2682.9	3261.94	

2.2. Numerical solution of the vibration-rotation Schrödinger equation of heteronuclear diatomic molecules

Since the radial function $P(R)$ is a solution of the equation [2, 8]

$$\frac{-\hbar^2}{2\mu}\left[P''(R) + \frac{2}{R}P'(R)\right] + \frac{J(J+1)\hbar^2}{2\mu R^2}P(R) + U(R)P(R) = E_{\text{int}}P(R), \tag{20}$$

the vibration-rotation Schrödinger equation with Varshni (III) potential function will be

$$\frac{-\hbar^2}{2\mu}\left(P''(r) + \frac{2}{r}P'(r)\right) + \left[\frac{J(J+1)\hbar^2}{2\mu\, r^2} + D_e\left[1 - \frac{r_e}{r}e^{-\beta(r^2 - r_e^2)}\right]^2\right]P(r) = EP(r), \tag{21}$$

therefore

$$\frac{-\hbar^2}{2\mu}F'' + \left[\frac{J(J+1)\hbar^2}{2\mu\, r^2} + D_e\left[1 - \frac{r_e}{r}e^{-\beta(r^2 - r_e^2)}\right]^2\right]F = EF. \tag{22}$$

then, the dimensionless form of this equation will be

$$F_r'' = \left(\frac{J(J+1)}{r_r^2} + 2D_{e,r}\left[1 - \frac{r_{e,r}}{x_r + r_{e,r}}e^{-(x_r^2 + 2x_r r_{e,r})}\right]^2 - 2E_r\right)F_r. \tag{23}$$

from (13) it follows that, dimensionless expression of G_r will be

$$G_r = \frac{J(J+1)}{r_r^2} + 2D_{e,r}\left[1 - \frac{r_{e,r}}{x_r + r_{e,r}} e^{-(x_r^2 + 2x_r r_{e,r})}\right]^2 - 2E_r . \qquad (24)$$

Comparing (24) and (14) we find out that the difference between the vibrational G_r and the vibration-rotation G_r is only in the term $J(J+1)/r_r^2$. So, we can obtain the vibration-rotation G_r for all potentials by adding the term $J(J+1)/r_r^2$ to vibrational G_r , and solve the related Schrödinger equation numerically as before. Finally, we obtain the vibration-rotation energy levels of the molecule. Tables 4 and 5, demonstrate the calculated vibration-rotation energy levels of the IF molecule for the two initial vibrational states ($v=0$ and $v=1$).

Table 4
Rotational levels for vibrational state $v=0$ of the IF molecule in terms of cm^{-1}.

Potential	$E_{v,J}$					
	$E_{0,0}$	$E_{0,1}$	$E_{0,2}$	$E_{0,3}$	$E_{0,4}$	$E_{0,5}$
Morse	304.3436	304.9027	306.0411	307.6978	309.9224	312.7544
Rydberg	304.3891	304.9482	306.0625	307.7848	309.9804	312.7765
Varshni(II)	304.2991	304.8583	305.9866	307.6581	309.8927	312.6826
Varshni(III)	304.4331	304.9824	306.1209	307.7886	310.0256	312.8222
Varshni(VI)	304.3633	304.9245	306.0489	307.7188	309.9853	312.7213
Poschl-Teller	304.3511	304.9102	306.0386	307.7122	309.942	312.7389
Lippincott	303.9794	304.5386	305.6872	307.3448	309.5728	312.3682
Hulburt-Hirschfelder	304.3812	304.9403	306.0687	307.7364	309.9986	312.749
Frost-Musulin	304.3616	304.9206	306.0488	307.7191	309.9684	312.7429
Linnet	304.5278	305.0871	306.2255	307.8863	310.1244	312.9168
Rosen-Morse	304.344	304.9032	306.0316	307.7093	309.9386	312.7345

Table 5
Rotational levels for vibrational state $v=1$ of the IF molecule in terms of cm^{-1}.

Potential	$E_{v,J}$					
	$E_{1,0}$	$E_{1,1}$	$E_{1,2}$	$E_{1,3}$	$E_{1,4}$	$E_{1,5}$
Morse	908.3837	908.9429	910.0613	911.7388	913.9756	916.7715
Rydberg	908.9551	909.5143	910.6326	912.3101	914.5468	917.3426
Varshni(II)	907.6058	908.165	909.2833	910.9608	913.1975	915.9933
Varshni(III)	909.4955	910.0548	911.1733	912.8511	915.0882	917.8846
Varshni(VI)	909.0096	909.5688	910.6872	912.3648	914.6016	917.3976
Poschl-Teller	908.4116	908.9707	910.0891	911.7667	914.0035	916.7994
Lippincott	909.3626	909.9219	911.0403	912.7181	914.9551	917.7513
Hulburt-Hirschfelder	908.3633	908.9225	910.0409	911.7185	913.9552	916.7512
Frost-Musulin	908.4998	909.0589	910.1771	911.8544	914.0907	916.8862
Linnet	909.8416	910.4009	911.5195	913.1973	915.4343	918.2307
Rosen-Morse	908.5784	909.1376	910.2561	911.9338	914.1707	916.9669

2.3. Determination of ω_e and $\omega_e x_e$ from vibrational levels

As we know, vibrational energy of an anharmonic oscillator is as follows [27, 28]:

$$\frac{E_v}{hc} = Q(v) = \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 + ... \qquad (25)$$

where ω_e is vibration wavenumber and $\omega_e x_e$ and $\omega_e y_e$ are anharmonicity constants.

The distance between the two vibrational adjacent levels is obtained from the following relation:

$$\Delta Q_v = Q(v+1) - Q(v). \tag{26}$$

thus:

$$\Delta Q_v = \omega_e - \omega_e x_e (2v+2) + \omega_e y_e \left(\frac{26}{8} - 3v^2 - 6v \right) + ..., \tag{27}$$

which becomes finally as follows:

$$\Delta Q_v \approx \omega_e - \omega_e x_e (2v+2). \tag{28}$$

Therefore, to determine ω_e and $\omega_e x_e$, it should be clear at least three vibrational levels. Now for example, we compute ω_e and $\omega_e x_e$ of the IF molecule with Varshni(III) potential function. Wavenumbers of vibrational jumps of the IF molecule with Varshni(III) potential function are shown in Table 6.

According to the relation (28), if we draw the diagram ΔQ_v in terms of $(2v+2)$, it will obtain a straight line which gives slope $-\omega_e x_e$ and y-intercept, ω_e. According to this method, for the IF molecule with Varshni(III) potential function, we obtain $\omega_e = 610.7818$ cm^{-1} and $\omega_e x_e = 2.7768$ cm^{-1}.

Table 6
Wavenumbers of vibrational jumps of the IF molecule with Varshni (III) potential function.

$(v+1)-v$	$(2v+2)$	ΔQ in terms of cm^{-1}
1-0	2	605.0624
2-1	4	599.7595
3-2	6	594.2849
4-3	8	588.6461
5-4	10	582.8507

2.4. Determination of B_e and α_e from vibration-rotation levels

Vibration-rotation energy of anharmonic oscillators is as follows [30-32]:

$$\varepsilon_{v,J} = Q(v) + F_v(J) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + ... + B_v J(J+1) - D_v J^2 (J+1)^2 + ... \tag{29}$$

As we know, the selection rule of $\Delta J = \pm 1$ ruling over transitions between rotational levels results in a branch R $(\Delta J = +1)$ and a branch P $(\Delta J = -1)$. Each transition becomes marked with $R(J)$ or $P(J)$.

In many cases, because of inequality of B' and B'', the bands of the branches R and P are asymmetric. To obtain B' and B'' from spectral data, we use combination differences method. If we need to obtain some information about one series of lower states or one series of upper ones between which the transitions are occurred, then according to this method, the difference between wavenumber of transitions with common upper state, only depends upon the characteristics of lower state. Likewise, the difference between wavenumber of transitions with common lower state only depends upon the characteristics of the upper state.

As we know, in case of a vibration-rotation band, the lines $R(0)$ and $P(2)$ have got a common upper state with $J'=1$ and as a result, $\tilde{\nu}[R(0)]-\tilde{\nu}[P(2)]$ is only a function of B''. The transitions $R(1)$ and $P(3)$ are common in $J'=2$. Hence, we can say that in general $\tilde{\nu}[R(J-1)]-\tilde{\nu}[P(J+1)]$ that is written as $\Delta_2''F(J)$, is only a function of B''. For these transitions, we have:

$$\begin{aligned}\Delta_2''F(J)=\tilde{\nu}[R(J-1)]-\tilde{\nu}[P(J+1)]&=\left[\tilde{\nu}_0+B'J(J+1)-B''J(J-1)-D'J^2(J+1)^2+D''J^2(J-1)^2\right]\\&-\left[\tilde{\nu}_0+B'J(J+1)-B''J(J+1)(J+2)-D'J^2(J+1)^2+D''J^2(J+1)^2(J+2)^2\right]\\&=(4B''-6D'')(J+\frac{1}{2})-8D''(J+\frac{1}{2})^3.\end{aligned} \tag{30}$$

Thus, the diagram of changes $\Delta_2''F(J)/(J+1/2)$ in terms of $(J+1/2)^2$, gives a line with the slope $-8D''$ and y-intercept $(4B''-6D'')$. As the two $R(J)$ and $P(J)$ are common in low states, therefore $\tilde{\nu}[R(J)]-\tilde{\nu}[P(J)]$ is only a function of B'. So we will have:

$$\begin{aligned}\Delta_2'F(J)=\tilde{\nu}[R(J)]-\tilde{\nu}[P(J)]&=\left[\tilde{\nu}_0+B'(J+1)(J+2)-B''J(J+1)-D'(J+1)^2(J+2)^2+D''J^2(J+1)^2\right]\\&-\left[\tilde{\nu}_0+B'J(J-1)-B''J(J+1)-D'J^2(J-1)^2+D''J^2(J+1)^2\right]\\&=(4B'-6D')(J+\frac{1}{2})-8D'(J+\frac{1}{2})^3.\end{aligned} \tag{31}$$

Thus, the diagram of changes $\Delta_2'F(J)/(J+1/2)$ in terms of $(J+1/2)^2$, gives a line with the slope $-8D'$ and y-intercept $(4B'-6D')$. By regarding the relations (30) and (31) and also the Tables 4 and 5, the values B_0 and B_1 for the IF molecule with Varshni(III) potential function are 0.281226 and 0.279636, respectively. According to the relation [30]:

$$B_v=B_e-\alpha\left(v+\frac{1}{2}\right), \tag{32}$$

Table 7

Spectroscopic constants of the IF molecule for all potential functions and deviation percentages from experimental values.

Potential	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	%error(av)
Morse	610.3179323	3.127228291	0.282011202	0.001610499	-3.24623872
Rydberg	610.2920599	2.855192337	0.283067969	0.002324512	4.19364745
Varshni(II)	610.0635947	3.412313365	0.28180642	0.001482443	-2.69913534
Varshni(III)	610.781762	2.776840816	0.282022327	0.001590858	-6.29588047
Varshni(VI)	610.3198872	2.825683996	0.282108683	0.001672717	-4.82356128
Poschl-Teller	610.2436233	3.090876958	0.281869279	0.001515884	-4.81558776
Lippincott	610.3398071	2.464203711	0.285706693	0.004056236	24.4029689
Hulburt-Hirschfelder	610.2950543	3.14790117	0.282216684	0.001747487	-1.23548709
Frost-Musulin	610.2711679	3.059656064	0.281896637	0.001568289	-4.36299498
Linnet	610.2013369	2.444552229	0.283332987	0.002465441	2.80348402
Rosen-Morse	610.3298391	3.034542904	0.282275484	0.001771445	-1.81748346
Experimental	610.24	3.12	0.2797111	0.0018738	

B_e and α_e become $0.28202\,\mathrm{cm}^{-1}$ and $0.001591\,\mathrm{cm}^{-1}$, respectively. Similarly, B_e and α_e are computed for other heteronuclear diatomic molecules with other potential functions. The gained results for the IF molecule are inserted in Table 7.

3. Conclusions

In this paper, the nuclear Schrödinger equation for the IF molecule is solved by the Numerov method. The potential functions of Morse, Rydberg, Varshni(II), Varshni(III), Varshni(VI), Poschl-Teller, Hulburt-Hirschfelder, Lippincott, Frost-Musulin, Linnet, and Rosen-Morse are used to calculate the quantum states, vibrational energy levels, and vibration-rotation energy levels. The results are compared with the available experimental values and the accuracy of these potential functions is estimated. Our calculations have utilized more than 200 worksheets of Excel spreadsheet software. Then the spectroscopic constants ω_e, $\omega_e x_e$, B_e, and α_e were computed from vibrational and vibration-rotation energy levels. To compute according to this method, 5 Excel worksheets are used for the IF molecule with all of the potential functions. The Hulburt-Hirshfelder potential function in comparison with other potential functions, forecast the values of the spectroscopic constants with a higher accuracy. Totally, the spectroscopic constants gained from this method, are in a very good accordance with experimental values.

Appendix (A)

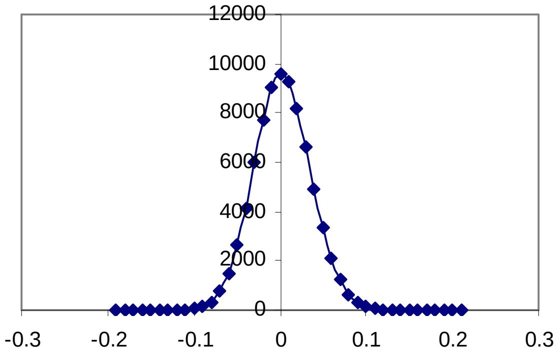
Programming by the Excel spreadsheet to obtain vibrational levels for the IF molecule with Varshni (III) potential function is as follows (the operations to be done in each cell are written in front of each cell):

A1: Write Potential Function (U = D_e*[1- r_e/r *EXP(-β*(r^2-r_e^2)]^2)
A3: Write ($E_{vib,r}$=)
B3: Enter $E_{vib,r,guess}$
C3: Write (S_r=)
D3: Write (0.01)
A5: Write (x_r)
B5: Write (G_r)
C5: Write (Psi_r)
A7: Write (-0.19)
A8: Write (A7+$D$3)
A9-A47: Copy A8, Select A9-A47, Paste A8 in A9-A47
B7: Write (=2*46397.2898*(1-1.0778/(A7+1.0778)*EXP(-(A7^2+2*A7*1.0778)))^2-2*$B$3)
B8-B47: Copy B7, Select B8-B47, Paste B7 in B8-B47
C7: Write (0)
C8: Write (1E-4)
C9: Write (=(2*C8-C7+5*B8*C8*$D$3^2/6+B7*C7*$D$3^2/12)/(1-B9*$D$3^2/12))
C10-C47: Copy C9, Select C10-C47, Paste C9 in C10-C47
D9: Write (=IF(C9*C8〈0; 1; 0))
D10-D47: Copy D9, Select D10-D47, Paste D9 in D10-D47
E3: Write (Nodes=)
F3: Write (=SUM(D9:D47))
E5: Write ($nPsi_r$)
E50: Write (=SUMSQ(C7:C47)*$D$3)
E7: Write (=C7/$E$50^0.5)
E8-E47: Copy E7, Select E8-E47, Paste E7 in E8-E47
G3: Write (Psi_r Max=)

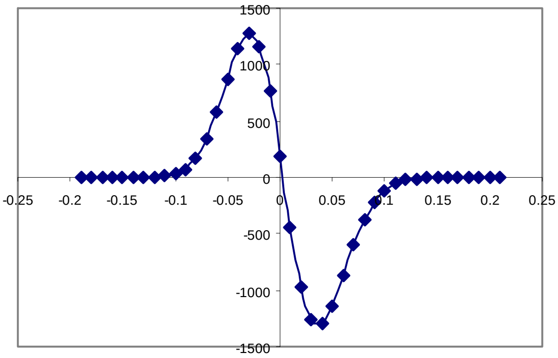
H3: Write (=$E$47)
J3: Write (E_{vib}=)
K3: Write (=$B$3*0.64968)

Appendix (B)

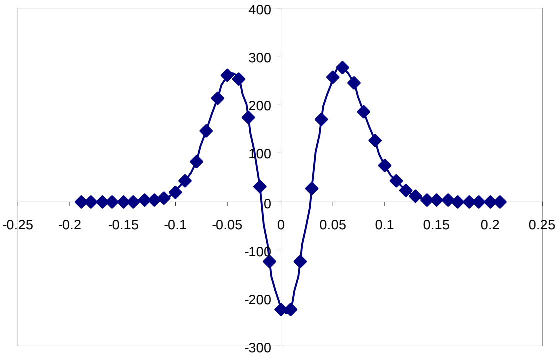
The graphs of six lower vibrational wave functions versus x_r for IF molecule with varshni(III) potential function.



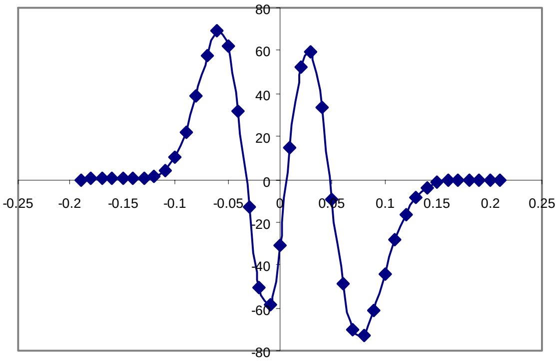
ψ_0



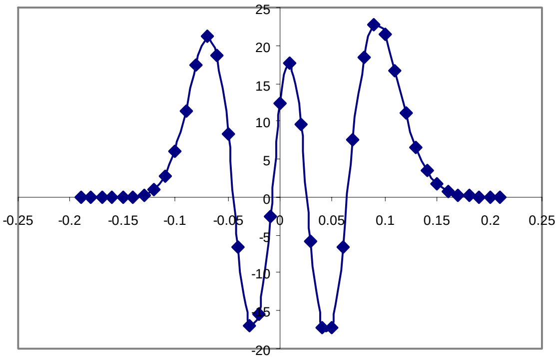
ψ_1



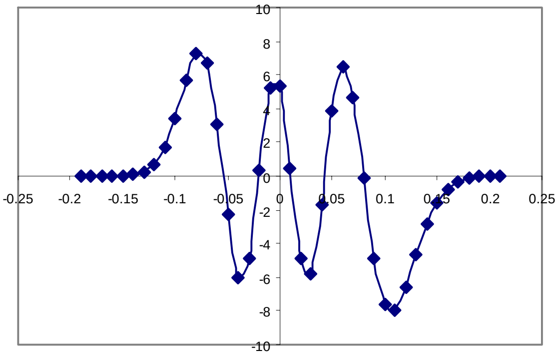
ψ_2



ψ_3



ψ_4



ψ_5

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References

[1] E.U. Condon, Science 83 (1936) 105.
[2] I.N. Levine, Quantum Chemistry, 5th ed., Prentice Hall, 2000.
[3] E.C. Kemble, Rev. Mod. Phys. 1 (1929) 157.
[4] C. Deng, R. Zhang, D. Feng, Int. J. Quant. Chem. 45 (1993) 385.
[5] W.H. Shaffer, H.H. Nielsen, Phys. Rev. 56 (1939) 188.

[6] M. Born, J.R. Oppenheimer, Ann. Phys. 84 (1927) 457.
[7] N. Zettili, Quantum Mechanics, Wiley, England, 2001.
[8] J.P. Lowe, K.A. Peterson, Quantum Chemistry, 3th ed, Elsevier Academic Press, San Diego, 2006.
[9] S. Ivanov, Theoretical and Quantum Mechanics, Springer, Netherland, 2006.
[10] C.L. Yang, Z.H. Zhu, R. Wang, X.Y. Lin, J. Mol. Struct. (Theochem) 548 (2001) 47.
[11] A.A. Al-Saadi, N. Meinander, J. Laane, J. Mol. Spect. 242 (2007) 17.
[12] F. Gao, C.L. Yang, T.Q. Ren, J. Mol. Struct. (Theochem) 758 (2006) 81.
[13] A.A. Zavitsas, J. Mol. Spect. 221 (2003) 67.
[14] V. Špirko, R. Polák, J. Mol. Spect. 248 (2008) 77.
[15] R. Wang, Z.H. Zhu, C.L. Yang, J. Mol. Struct. (Theochem) 571 (2001) 133.
[16] S. Noorizadeh, G.R. Pourshams, J. Mol. Struct. (Theochem) 678 (2004) 207.
[17] A.A. Zavitsas, J. Mol. Spect. 236 (2006) 168.
[18] A.T. Royappa, V. Suri, J.R. McDonongh, J. Mol. Struct. 787 (2006) 209.
[19] P.M. Morse, Phys. Rev. 34 (1929) 57.
[20] R.Z. Rydberg, Fur Physik. 73 (1931) 376.
[21] Y.P. Varshni, Rev. Mod. Phys. 29 (1957) 664.
[22] G. Poschl, E. Teller, Z. Physik. 83 (1933) 143.
[23] H.M. Hulburt, J.O. Hirschfelder, J. Chem. Phys. 9 (1941) 611.
[24] A.A. Frost, B. Musulin, J. Chem. Phys. 22 (1954) 1017.
[25] J.W. Linnet, Trans. Faraday Soc. 36 (1940) 1123; 38 (1942) 1.
[26] E.R. Lippincott, J. Chem. Phys. 21 (1953) 2070.
[27] N. Rosen, P.M. Morse, Phys. Rev. 42 (1932) 210.
[28] Y.P. Varshni, Chem. Phys. 342 (2007) 297.
[29] G. Herzberg, Spectra of Diatomic Molecules, 2th ed., Van Nostrand Reinhold Company, Netherland, 1950.
[30] J.M. Hollas, Modern Spectroscopy, 4th ed., Wiley, England, 2004.
[31] G. Aruldhas, Molecular Structure and Spectroscopy, Prentice Hall, India, 2004.
[32] J.M. Brown; A. Carrington, Rotational Spectroscopy of Diatomic Molecules, Cambridge University Press, UK, 2003.