Accurate studies on the full vibrational energy spectra and molecular dissociation energies for some electronic states of halogen molecule*

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This paper obtains accurate vibrational spectroscopic constants and full vibrational energy spectrum by the algebraic method (AM) for some electronic states of halogen diatomic molecules. Motivated by the recent success of obtaining the dissociation energies of Li_2 molecule by using a new analytical formula, it further extends the formula to study the dissociation energies of halogen diatomic molecules. The results show that the AM spectrum and the theoretical dissociation energies agree well with RKR data and experimental data respectively.

Keywords: vibrational energy, dissociation energy, halogen molecule, algebraic method

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1. Introduction

The studies of the vibrational spectrum $\{E_\upsilon\}$ and molecular dissociation energy $D_{\rm e}$ of the diatomic molecular electronic states have drawn considerable attention,[1,2] since they play a very crucial role in the studies of molecular potentials, molecular structures, molecular scattering and molecular dissociation. It is customary to represent theoretically correct vibrational/rovibrational energy $E_\upsilon/E_{\upsilon J}$ of a diatomic system in an infinite series of Duham's form[3] or Herzberg's form[4,5] using perturbation theory, but the accurate high-lying $E_\upsilon/E_{\upsilon J}$ are usually difficult to obtain for many systems due to either experimental limitations or theoretically lacking correct high order terms of nonharmonic vibrational/rovibrational constants (energy expansion coefficients). However, if we want to obtain molecular dissociation energy $D_{\rm e}$ by using the Birge–Sponer (B–S)[6] extrapolation process or the LeRoy–Bernstein (LRB)[7] method, the high-lying vibrational energies E_υ near diatomic dissociation limit are necessary.

The halogen diatomic molecules are one of the most studied diatomic molecules, and have attracted the interest of many experimentalists, mainly because it has a relatively simple electronic structure, and electronic transitions in the visible range present an excellent test case molecule for development of new experimental and theoretical methods in laser spectroscopy and molecular dynamics. Since the first tentative vibrational analysis of the bromine visible bands was finished by Kuhn in 1926,[8] numerous studies have been devoted to the improvement of the spectroscopic knowledge both from a theoretical and an experimental point of view. Significant progress has been made on the spectroscopy of the halogen molecules. In 1981, Sur and Tellinghuisen calculated Rydberg–Klein–Rees (RKR) potentials ($\upsilon_{\max} = 23, E_{\upsilon_{\max}} = 2504.15$ cm^{-1}) by using the spectroscopic expansion parameters, and obtained dissociation energies ($D_{\rm e} = 2835$ cm^{-1}) by long-range theory[9] for the $2{\rm u}^3\Pi$ state of Br_2. In addition, optical–optical double-resonance[10−15] technique has extensively been used for studying the spectroscopy of the halogen molecules, also. Several spectroscopic investigations have been devoted to some electronic state of halogen molecules, such as, Focsa, Li *et al.*[16] gave high-lying vibrational levels ($\upsilon_{\max} = 29$, $E_{\upsilon_{\max}} = 8589.8067$ cm^{-1}) by laser-induced fluorescence Fourier transform spectroscopy[16,17] for the $X^1\Sigma_{\rm g}^+$ state of Br_2 in 2000.

However, these methods still have defects. The rotational structure in almost all the bands is heavily congested, this makes an unambiguous assignment of the rotational lines difficult to obtain. For example,

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the final assignments include nearly 1500 rotational lines and bandheads for the $2u^3\Pi$ state of Br_2. Theoretically, conventional formulas, Duham's form and Herzberg's form are not valid for levels near the dissociation limit. In order to overcome these problems, we describe the algebraic method (AM) in detail in this paper.

In the present work, the AM is applied to study the accurate full vibrational energy spectra $\{E_\upsilon\}$ of four electronic states of halogen molecules, which is successfully used in the preceding paper.[5,18,19] Results are listed in Table 3. Subsequently, we calculate the dissociation energies D_e of these states by using the new formula Eq. (23). As can be seen from the Table 1 and Table 2, the theoretical dissociation energies agree excellently with experimental data.

The structure of the paper is as follows. In the second section we review AM for accurate vibrational spectrum. In the third section, following Ref. [20] we give an expression for dissociation energy. The final section contains application and analyses.

2. AM for accurate vibrational spectrum

In 2002, Sun W G *et al.* proposed an expression of the vibrational energies of a diatomic molecular electronic state, which is educed by using the second order perturbation theory for the nuclear potential. Following Ref. [5], this expression is written as

$$\begin{aligned} E_\upsilon = {} & \omega_0 + (\omega_\mathrm{e} + \omega_{e0})(\upsilon + \tfrac{1}{2}) - \omega_\mathrm{e}x_\mathrm{e}(\upsilon + \tfrac{1}{2})^2 \\ & + \omega_\mathrm{e}y_\mathrm{e}(\upsilon + \tfrac{1}{2})^3 + \omega_\mathrm{e}z_\mathrm{e}(\upsilon + \tfrac{1}{2})^4 \\ & + \omega_\mathrm{e}t_\mathrm{e}(\upsilon + \tfrac{1}{2})^5 + \omega_\mathrm{e}s_\mathrm{e}(\upsilon + \tfrac{1}{2})^6 \\ & + \omega_\mathrm{e}r_\mathrm{e}(\upsilon + \tfrac{1}{2})^7 + \cdots, \end{aligned} \tag{1}$$

where ω_0 is the vibrational constant for the zeroth order of $(\upsilon + 1/2)$ and corresponds to Dunham's Y_{00} term,[21] and $\omega_{\mathrm{e}0}$ is the correction to harmonic vibrational constant ω_e for the first order of $(\upsilon+1/2)$, which is similar to the well-known expression of Herzberg.[22] In Eq. (1), ω_0 and $\omega_{\mathrm{e}0}$ are new terms in comparison with the Herzberg's formula.

An AM has been successfully employed to calculate accurate vibrational constants and vibrational energies by limited experimental vibrational eigenvalues in our recent study.[20] Now we rewrite firstly Eq. (1) in matrix form as

$$AX = E, \tag{2}$$

where the solution of matrix X and the energy matrix E are

$$X = \begin{pmatrix} \omega_0 \\ \omega'_\mathrm{e} \\ -\omega_\mathrm{e}x_\mathrm{e} \\ \omega_\mathrm{e}y_\mathrm{e} \\ \vdots \\ \omega_\mathrm{e}r_\mathrm{e} \end{pmatrix},$$

$$E = \begin{pmatrix} E_\upsilon \\ E_{\upsilon+i} \\ E_{\upsilon+j} \\ \vdots \\ E_{\upsilon+s} \end{pmatrix}, \quad \upsilon = 0, 1, 2, \ldots. \tag{3}$$

In which there are 8 vibrational constants X, and $\omega'_\mathrm{e} = \omega_\mathrm{e} + \omega_{\mathrm{e}0}$. The matrix element of the coefficient matrix A in Eq. (2) is $A_{\upsilon k} = (\upsilon + \frac{1}{2})^k$ with $k = 0$, 1, 2, ..., 7.

Generally speaking, it is easier to obtain a subset $[E_\upsilon]$, of m energies of the full vibrational energy spectrum $\{E_\upsilon\}$ experimentally than to obtain the molecular dissociation energy D_e for many diatomic molecular electronic systems. In order to obtain directly the vibrational constants in X, for such a situation, we can choose Q groups of energies out of the m energies of the subset. If we solve Eq. (2) Q times, we will obtain Q sets of vibrational constants $[X]$. If the energy spectrum $\{E_{\upsilon,\mathrm{cal}} \equiv E_\upsilon\}$ is generated by using a solution vector X of the Q sets solutions, then it best satisfies the following conditions:

$$\overline{\Delta E(e,c)} = \sqrt{\frac{1}{m}\sum_{\upsilon=0}^{m-1} |E_{\upsilon,\mathrm{exp}} - E_{\upsilon,\mathrm{cal}}|^2} \to 0, \tag{4}$$

$$\Delta E(\upsilon_\mathrm{max}, \upsilon_\mathrm{max} - 1) = E_{\upsilon_\mathrm{max}} - E_{\upsilon_\mathrm{max}-1} \to \text{small enough}, \tag{5}$$

$$D_\mathrm{e} - E_{\upsilon_\mathrm{max}} < E_{\upsilon_\mathrm{max}} - E_{\upsilon_\mathrm{max}-1}. \tag{6}$$

It indicates that this full AM spectrum $\{E_v\}$ will be an excellent representation of the true eigenvalue set $\{E_{v,\mathrm{exp}}\}$ of an electronic state, whose subset of all higher vibrational energies $\{E_{v',\mathrm{exp}}; \nu' \geq m\}$ may be difficult to obtain experimentally. The quality of the AM spectrum $\{E_v\}$ directly depends on the accuracy of the energy group chosen from the known subset $[E_{v,\mathrm{exp}}]$. The harmonic vibrational constant ω_e may be obtained by using $\omega_\mathrm{e} = \omega'_\mathrm{e} - \omega_{\mathrm{e}0}$, the correction term $\omega_{\mathrm{e}0}$ may be calculated by using[5]

$$\begin{aligned}\omega_{\mathrm{e}0} = & -\frac{95}{8\omega_\mathrm{e}}b_3b_5f_3f_5 - \frac{67}{16\omega_\mathrm{e}}b_4^2f_4^2 + \frac{25}{8}b_6f_6 \\ & - \frac{19277}{256\omega_\mathrm{e}}b_6^2f_6^2 - \frac{22029}{128\omega_\mathrm{e}}b_5b_7f_5f_7 \\ & - \frac{10521}{64\omega_\mathrm{e}}b_4b_8f_4f_8 - \frac{5450499}{2048\omega_\mathrm{e}}b_8^2f_8^2. \end{aligned} \quad (7)$$

In Eq. (7) the expansion coefficients b_n have the general form as shown in Refs. [5] and [18], and the vibrational force constants f_n can be evaluated by means of potential variational method (PVM) suggested in Ref. [5].

The vibrational constants obtained by using Eq. (2) should be one of the best physical representations of the true vibrational spectroscopic constants in the specified molecular system. Because of making not any mathematical approximations or using physical models, if the experimental energies in the subset $[E_v]$ have a high enough accuracy, the so obtained AM vibrational spectroscopic constants:

$$\begin{aligned}X = \{&\omega_0, \omega_\mathrm{e} + \omega_{\mathrm{e}0}, -\omega_\mathrm{e}x_\mathrm{e},\ \omega_\mathrm{e}y_\mathrm{e}, \\ &\omega_\mathrm{e}z_\mathrm{e},\ \omega_\mathrm{e}t_\mathrm{e},\ \omega_\mathrm{e}s_\mathrm{e},\ \omega_\mathrm{e}r_\mathrm{e}\}\end{aligned}$$

and the resulting vibrational energy spectrum $\{E_v\}$ should not only reproduce all known experimental vibrational energies but also correctly produce all high-lying vibrational energies in the full vibrational spectrum $\{E_v\}$. Such as, we will obtain the correct maximum vibrational energy E_{v_max} of some diatomic molecular electronic states.

3. Analytical expression for molecular dissociation energy

LeRoy and Bernstein have proposed the first-order WKB (Wentzel–Kramers–Brillouin) quantum condition for the eigenvalues of a diatomic potential $V(R)$,[7] as follows:

$$v + \frac{1}{2} = \frac{(2\mu)^{1/2}}{\pi\hbar}\int_{R_1(v)}^{R_2(v)}[E_v - V(R)]^{1/2}\mathrm{d}R, \quad (8)$$

where μ is the reduced mass, $V(R)$ vibrational potential, E_v the vibrational energy with vibrational quantum number v, both $R_1(v)$ and $R_2(v)$ are the classical turning points of the energy E_v. Differentiating Eq. (8), with respect to E_v, we obtain

$$\begin{aligned}\frac{\mathrm{d}v}{\mathrm{d}E_v} = & (\pi\hbar)^{-1}\left(\frac{1}{2}\mu\right)^{1/2} \\ & \times \int_{R_1(v)}^{R_2(v)}[E_v - V(R)]^{-1/2}\mathrm{d}R. \end{aligned} \quad (9)$$

If the vibrational potential $V(R)$ is replaced by a good approximate function which is accurately close to the outer turning point $R_2(v)$ of $V(R)$, the integral of Eq. (9) will be nearly unchanged. Now the asymptotic expression near dissociation limit for such a good function has been chosen by LRB[7] as

$$V(R) = D_\mathrm{e} - \frac{C_n}{R^n}, \quad (10)$$

where D_e is the dissociation energy of a molecular system, which is the dissociation limit of the diatomic potential, the potential coefficient C_n is given by[7]

$$E_v = D_\mathrm{e} - \frac{C_n}{[R_2(v)]^n}. \quad (11)$$

Transforming the integration variable : $y = R_2(v)/R$, Eq. (9) we have

$$\begin{aligned}\frac{\mathrm{d}v}{\mathrm{d}E_v} = & -(\pi\hbar)^{-1}\left(\frac{1}{2}\mu\right)^{1/2}\frac{C_n^{1/n}}{[D_\mathrm{e} - E_v]^{(1/2+1/n)}} \\ & \times \int_1^{R_2/R_1} y^{-2}\left(y^n - 1\right)^{-1/2}\mathrm{d}y. \end{aligned} \quad (12)$$

when the limit $R_2(v)/R_1(v) \to \infty$ (i.e., $R_2(v) \to \infty$) near the dissociation limit, $\mathrm{d}E_v/\mathrm{d}v$ is given by[17]

$$\begin{aligned}\frac{\mathrm{d}E_v}{\mathrm{d}v} = & \hbar\left(\frac{2\pi}{\mu}\right)^{1/2}\frac{\Gamma(1+1/n)}{\Gamma(1/2+1/n)} \\ & \times \frac{n}{C_n^{1/n}}[D_\mathrm{e} - E_v]^{[(n+2)/2n]} \\ = & K_n[D_\mathrm{e} - E_v]^{[(n+2)/2n]}. \end{aligned} \quad (13)$$

Equation (13) shows that for the high-lying vibrational states near molecular dissociation limit of a given diatomic system, the energy interval depends only on the long-range potential data D_e, n, and C_n. Regarding the leading dispersion coefficient C_2, $n = 2$, from Eqs. (12) and (13) we can obtain[7]

$$D_\mathrm{e} - E_v = [D_\mathrm{e} - E_0]\exp\left[-\pi\hbar v\left(\frac{2}{\mu C_2}\right)^{1/2}\right]. \quad (14)$$

Using Eq. (13) and its derivative, we have[7]

$$D_{\rm e} = E_\upsilon - \left(\frac{n+2}{2n}\right)\frac{[E'_\upsilon]^2}{E''_\upsilon}. \tag{15}$$

Equation (15) is an important intermediate result for $D_{\rm e}$. In order to obtain an applicable expression for molecular dissociation energy, we can take the first-order and the second-order derivatives respectively for the E_υ in Eq. (14) with respect to υ, and obtain

$$\begin{aligned} E'_\upsilon &= \frac{{\rm d}E_\upsilon}{{\rm d}\upsilon} = (\pi\hbar)\left(\frac{2}{\mu C_2}\right)^{1/2}[D_{\rm e} - E_0] \\ &\quad \times \exp\left[-\pi\hbar\upsilon\left(\frac{2}{\mu C_2}\right)^{1/2}\right], \qquad (16) \\ E''_\upsilon &= \frac{{\rm d}^2E_\upsilon}{{\rm d}\upsilon^2} = -(\pi\hbar)^2\left(\frac{2}{\mu C_2}\right)[D_{\rm e} - E_0] \\ &\quad \times \exp\left[-\pi\hbar\upsilon\left(\frac{2}{\mu C_2}\right)^{1/2}\right]. \qquad (17) \end{aligned}$$

Thus

$$\frac{E'_\upsilon}{E''_\upsilon} = -(\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}. \tag{18}$$

Near molecular dissociation limit, the high-lying vibrational energies are congestion. We may use the following approximation to substitute the energy derivative:

$$E'_\upsilon = \frac{{\rm d}E_\upsilon}{{\rm d}\upsilon} \approx \frac{1}{2}[E_{\upsilon+1} - E_{\upsilon-1}] + \cdots. \tag{19}$$

Now substituting Eqs. (18) and (19) into Eq. (15), we obtain the following analytical expression:

$$D_{\rm e}^{\rm cal} = E_\upsilon + \frac{1}{2}\left(\frac{n+2}{2n}\right)[E_{\upsilon+1} - E_{\upsilon-1}](\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}. \tag{20}$$

The vibrational states in Eq. (20) are those near the molecular dissociation limit according to the above reasoning. Subsequently, taking $\upsilon + 1 = \upsilon_{\max}$, and we find that equation (20) becomes

$$D_{\rm e}^{\rm cal} = E_{\upsilon_{\max}-1} + \frac{1}{2}\left(\frac{n+2}{2n}\right)[E_{\upsilon_{\max}} - E_{\upsilon_{\max}-2}](\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}. \tag{21}$$

Equation (21) can be expressed as

$$D_{\rm e}^{\rm cal} = E_{\upsilon_{\max}-2} + \frac{1}{2}\left(\frac{n+2}{2n}\right)[E_{\upsilon_{\max}-1} - E_{\upsilon_{\max}-3}](\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}. \tag{22}$$

Subtracting Eq. (22) from Eq. (21) we have

$$0 = [E_{\upsilon_{\max}-1} - E_{\upsilon_{\max}-2}] + \frac{1}{2}\left(\frac{n+2}{2n}\right)(\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}\{[E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}] - [E_{\upsilon_{\max}-2} - E_{\upsilon_{\max}-3}]\}.$$

Thus

$$\begin{aligned} &\frac{1}{2}\left(\frac{n+2}{2n}\right)(\pi\hbar)^{-1}\left(\frac{1}{2}\mu C_2\right)^{1/2}\{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}\} = \Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}, \\ &\frac{1}{2}\left(\frac{1}{2}\mu C_2\right)^{1/2} = \frac{2(2n)}{n+2}(\pi\hbar)\frac{\Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}}{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}, \\ &C_2 = \frac{2}{\mu}\left\{\left(\frac{2n}{n+2}\right)\frac{2\pi\hbar\Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}}{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}\right\}^2, \\ &C_2 = \frac{2}{\mu}\left(\frac{2n}{n+2}\cdot 2\pi\hbar\right)^2\left\{\frac{\Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}}{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}\right\}^2, \\ &C_2^{1/2} = 2\pi\hbar\left(\frac{2n}{n+2}\right)\left(\frac{2}{\mu}\right)^{1/2}\left(\frac{2n}{n+2}\cdot 2\pi\hbar\right)^2\left\{\frac{\Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}}{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}\right\}. \end{aligned}$$

Thus, one obtains a new analytical formula for dissociation energy

$$D_{\rm e}^{\rm cal} = E_{\upsilon_{\max}-1} + [E_{\upsilon_{\max}} - E_{\upsilon_{\max}-2}]\frac{\Delta E_{\upsilon_{\max}-1,\upsilon_{\max}-2}}{\Delta E_{\upsilon_{\max}-2,\upsilon_{\max}-3} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}. \tag{23}$$

Equation (23) indicates that for a diatomic molecular electronic state, if one knows the correct values of its four highest vibrational energies $E_{\upsilon_{\max}}$, $E_{\upsilon_{\max}-1}$, $E_{\upsilon_{\max}-2}$ and $E_{\upsilon_{\max}-3}$, then one can obtain straight forwardly the correct molecular dissociation energy $D_{\rm e}^{\rm cal}$. Since the right-hand side of Eq. (19) is always smaller than the left-hand side by a very small quantity, the $D_{\rm e}^{\rm cal}$ generated by using equation (23) will be a little smaller than the correct experimental dissociation energy $D_{\rm e}^{\rm exp}$,

$$D_{\rm e}^{\rm cal} < D_{\rm e}^{\rm exp}. \tag{24}$$

If equation (24) is violated, the $D_{\rm e}^{\rm cal}$, calculated by the four highest vibrational energies, are in error.

4. Application and analyses

The AM method[5] outlined in Section 2 has been applied to study the accurate vibrational full spectra $\{E_\upsilon\}$ for four electronic states for halogen molecule electronic states: $A'(2u^3\Pi)$ of I_2, $2u^3\Pi$ and $X^1\Sigma_g^+$ of Br_2, $2u^3\Pi$ of Cl_2, by using their corresponding incomplete experimental vibrational energy subset $[E_\upsilon]$. The vibrational spectroscopic constants (ω_0, $\omega_{\rm e0}$, $\omega_{\rm e}$, $\omega_{\rm e}x_{\rm e}$, $\omega_{\rm e}y_{\rm e}$, $\omega_{\rm e}z_{\rm e}$, $\omega_{\rm e}t_{\rm e}$, $\omega_{\rm e}s_{\rm e}$, $\omega_{\rm e}r_{\rm e}$), the maximum vibrational quantum numbers $\upsilon_{\max}$, the maximum AM vibrational energy $E_{\upsilon_{\max}}$ and the AM molecular dissociation energy $D_{\rm e}^{\rm cal}$ obtained by the proposed equation (23) are listed in Table 1. For comparison, Table 1 also gives vibrational spectroscopic constants from literature, and the corresponding $E_{\upsilon_{\max}}^{\Delta}$ [The last experimental vibrational energy]. The constant $\omega_{\rm e0}$ is calculated by using Eq. (7). It is easily found that our constants ($\omega_{\rm e}$) are in very good agreement with those in Ref. [23].

Table 2 presents the percent errors of experimental $D_{\rm e}^*$ with the AM $D_{\rm e}^{\rm cal}$ and the highest experimental vibrational energy $E_{\upsilon_{\max}}^{\Delta}$ given by literatures. Since AM depends only on the known accurate experimental energy subset $[E_\upsilon]$ to obtain the full energy spectrum $\{E_\upsilon\}$ and does not introduce any mathematical approximation and physical model in solving Eq. (2), the AM vibrational energy spectrum $\{E_\upsilon\}$ is accurate, and the highest AM vibrational energy $E_{\upsilon_{\max}}^{\rm AM}$ is in good agreement with experimental dissociation energy $D_{\rm e}^*$ in comparison with the maximum vibrational energy $E_{\upsilon_{\max}}^{\Delta}$ (with a "Δ" sign) obtained from experiment. Table 2 also shows that the AM dissociation energy $D_{\rm e}^{\rm cal}$ evaluated by using the AM vibrational energies and Eq. (23) is in very good agreement with experimental dissociation energy $D_{\rm e}^*$. For further comparison, we take $2u^3\Pi$ state of Br_2 as a typical example. the maximum vibrational quantum numbers $\upsilon_{\max}$ is only 23, obtained by Sur and Tellinghuisen[9] and the maximum AM vibrational energy $E_{\upsilon_{\max}}$ is 2504.15 $\rm cm^{-1}$ (see Table 3 of the present work). This value is far less than the experimental dissociation energies $D_{\rm e}^{\rm exp} = 2835$ $\rm cm^{-1}$.

Table 1. Vibrational spectroscopic constants, maximum vibrational quantum number $\upsilon_{\max}$, energies $E_{\upsilon_{\max}}$ and molecular dissociation energies $D_{\rm e}$ of some electronic states of halogen molecules (all quantities but $\upsilon_{\max}$ are in $\rm cm^{-1}$).

state		ω_0	$\omega_{\rm e0}$	$\omega_{\rm e}$	$\omega_{\rm e}x_{\rm e}$	$10^2\omega_{\rm e}y_{\rm e}$	$10^3\omega_{\rm e}z_{\rm e}$	$10^4\omega_{\rm e}t_{\rm e}$	$10^5\omega_{\rm e}s_{\rm e}$	$10^{10}\omega_{\rm e}r_{\rm e}$	$\upsilon_{\max}$	$E_{\upsilon_{\max}}$	$D_{\rm e}$
Br_2–$2u^3\Pi$	AM	0.0215384	−0.0814	165.123	−2.465	4.48936	−2.7827	−0.51654	0.5654	−835.789	34	2810.855	2831.532
	Ref. [9]			165.172	−2.504	5.689					23	2504.15	$2169.356^{\neq}$
	Ref. [9]												2835^*
Br_2–$X^1\Sigma_g^+$	AM	−0.00664	0.00035	325.3142	−1.078516	−0.20334	−0.011697	−0.007286	0.0003922	−0.803	75	15847.1696	15859.8
	Ref. [16]			325.314194	−1.078688	−0.19942	−0.01618				29	8589.8067	$32355.18^{\neq}$
	Ref. [16]												15894.55^*
Cl_2–$2u^3\Pi$	AM	0.007013	−0.0231	258.50	−5.434122	9.370513	−10.3865	0.585352	2.6605	−7468.034	22	3079.455	3105.476
	Ref. [23]			258.50	−5.458	10.5	−13.2				12	2395.527	$3884.597^{\neq}$
	Ref. [23]												3110^*
I_2–$A'(2u^3\Pi)$	AM	0.014098	−0.0323	106.070	−0.793	−3.8185	1.226	−0.3599	0.10125	−107.65	45	2461.938	2479.585
	Ref. [24]			106.07	−0.813	−3.315	0.6203				30	2075.09	$3158.496^{\neq}$
	Ref. [24]												2500^*

The $D_{\rm e}^*$ are experimental dissociation energies. The E^{Δ} and υ^{Δ} are the last experimental vibrational energy and available state respectively. The $D_{\rm e}^{\neq}$ are calculated by using vibrational spectroscopic constants from references.

Table 2. The percent energy errors $\Delta D_{\rm e}^{\rm cal}\%$, $\Delta D^{\neq}\%$ and $\Delta E^{\Delta}\%$ for four molecular electronic states, where, $\Delta D^{\rm cal}\% = 100 \times |D_{\rm e}^* - D_{\rm e}^{\rm AM}|/D_{\rm e}^*$, $\Delta D^{\neq}\% = 100 \times |D_{\rm e}^* - D_{\rm e}^{\neq}|/D_{\rm e}^*$, $\Delta E^{\Delta}\% = 100 \times |D_{\rm e}^* - E_{\upsilon_{\max}}^{\Delta}|/D_{\rm e}^*$.

state	$D_{\rm e}^*$	$D_{\rm e}^{\rm cal}$ (this work)	$\Delta D_{\rm e}^{\rm cal}\%$	$E_{\upsilon_{\max}}^{\Delta}$	$\Delta E^{\Delta}\%$	$D_{\rm e}^{\neq}$	$\Delta D^{\neq}\%$
Br_2–$2u^3\Pi$	2835[9]	2831.532	0.1223	2504.15	11.67	2169.3559	23.48
Br_2–$X^1\Sigma_g^+$	15894.55[16]	15859.8	0.218	8589.8067	45.96	32355.18	103.56
I_2–$A'(2u^3\Pi)$	2500[24]	2479.585	0.817	2075.09	16.996	3158.496	26.34
Cl_2–$2u^3\Pi$	3110[23]	3105.476	0.145	2395.527	22.97	3884.597	24.91

Table 3. Vibrational energy spectra for the ($2u^3\Pi$ and $X^1\Sigma_g^+$) states of Br_2, the ($2u^3\Pi$) state of I_2 and the ($2u^3\Pi$) state of Cl_2 (energies in cm^{-1}).

	Br_2				I_2		Cl_2	
υ	$2u^3\Pi$		$X^1\Sigma_g^+$		$2u^3\Pi$		$2u^3\Pi$	
	E_υ^{exp}	E_υ^{AM}	E_υ^{exp}	E_υ^{AM}	E_υ^{exp}	E_υ^{AM}	E_υ^{exp}	E_υ^{AM}
	Ref. [9]		Ref. [16]		Ref. [24]		Ref. [23]	
0	81.97	81.9700	162.3804	162.3804	52.83	52.830	127.898	127.898
1	242.29	242.2900	485.5306	485.5306	157.17	157.163	375.760	375.760
2	398.00	398.0000	806.505	806.5050	259.60	259.600	613.305	613.306
3	549.22	549.2287	1125.2909	1125.2909	359.96	359.961	840.642	840.642
4	696.03	696.0345	1441.8750	1441.8750	458.09	458.090	1057.693	1057.693
5	838.41	838.4100	1756.2437	1756.2437	553.85	553.847	1264.251	1264.251
6	976.29	976.2879	2068.3828	2068.3827	647.11	647.110	1460.028	1460.028
7	1109.55	1109.5506	2378.2777	2378.2776	737.78	737.772	1644.710	1644.710
8	1238.04	1238.0400	2685.9132	2685.9132	825.74	825.740	1818.011	1818.011
9	1361.57	1361.5700	2991.2737	2991.2737	910.93	910.935	1979.721	1979.721
10	1479.65	1479.9390	3294.3429	3294.3429	993.27	993.292	2129.766	2129.745
11	1592.98	1592.9431	3595.1037	3595.1038	1072.72	1072.760	2268.252	2268.129
12	1700.46	1700.3899	3893.5386	3893.5387	1149.25	1149.299	2395.527	2395.071
13	1802.23	1802.1110	4189.6294	4189.6294	1222.82	1222.886		2510.908
14	1898.14	1897.9745	4483.3568	4483.3568	1293.45	1293.512		2616.081
15	1988.09	1987.8960	4774.7011	4774.7010	1361.13	1361.184		2711.077
16	2072.03	2071.8479	5063.6415	5063.6412	1425.89	1425.924		2796.327
17	2149.99	2149.8673	5350.1565	5350.1559	1487.77	1487.770		2872.083
18	2222.06	2222.0600	5634.2235	5634.2225	1546.82	1546.778		2938.245
19	2288.43	2288.6035	5915.8189	5915.8175	1603.12	1603.019		2994.149
20	2349.36	2349.7452	6194.9181	6194.9163	1656.74	1656.584		3038.312
21	2405.26	2405.7975	6471.4954	6471.4933	1707.79	1707.577		3068.117
22	2436.64	2457.1289	6745.5237	6745.5214	1756.38	1756.123		3079.455
23	2504.15	2504.1500	7016.9750	7016.9726	1802.64	1802.356		
24		2547.2952	7285.8196	7285.8173	1846.71	1846.430		
25		2586.9982	7552.0265	7552.0247	1888.75	1888.506		
26		2623.6627	7815.5635	7815.5623	1928.93	1928.757		
27		2657.6254	8076.3966	8076.3960	1967.45	1967.361		
28		2689.1141	8334.4900	8334.4900	2004.50	2004.500		
29		2718.1971	8589.8067	8589.8067	2040.30	2040.352		
30		2744.7261		8842.3065	2075.09	2075.090		
31		2768.2708		9091.9475		2108.873		
32		2788.0451		9338.6860		2141.840		
33		2802.8247		9582.4754		2174.103		
34		2810.8554		9823.2669		2205.737		
...				...		...		
42				11634.8101		2424.337		
43				11845.9018		2441.907		
44				12053.3219		2454.854		
45				12256.9795		2461.938		
...				...				
72				15795.6325				
73				15823.5429				
74				15840.8787				
75				15847.1696				
D_e^{cal}		2831.532		15859.8240		2479.585		3105.476
D_e^{exp}		2835[9]		15894.5460[16]		2500[24]		3110[23]

However, we have obtained the maximum vibrational quantum numbers $\upsilon_{\max} = 34$, the maximum AM vibrational energy $E_{\upsilon_{\max}} = 2810.855$ cm^{-1} and accessed to the dissociation energies $D_{\rm e}^{\rm cal} = 2831.532$ cm^{-1} by using AM vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ and Eq. (23). The error of our results in comparison with the experimental data is only 0.1223%. For other three given electronic states, each of the dissociation energies was estimated by using the same method. The results show that all $D_{\rm e}^{\rm cal}$ satisfy Eq. (24).

Table 3 displays the AM vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ for each of the four electronic states and the corresponding available values from literatures. These results indicate that all the full AM vibrational spectra $\{E_\upsilon^{\rm AM}\}$ not only reproduce all known experimental vibrational energies $[E_\upsilon^{\rm exp}]$ in low-lying vibrational states, but also correctly generate all high-lying vibrational energies E_υ locating in molecular asymptotic and dissociation region. These high-lying vibrational energies may be difficult to obtain experimentally or quantum mechanically for many electronic systems. This is shown in Fig. 1 which plots all known experimental vibrational energies $[E_\upsilon^{\rm exp}]$ and the full AM vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ for the $X^1\Sigma_{\rm g}^+$ state of Br_2.

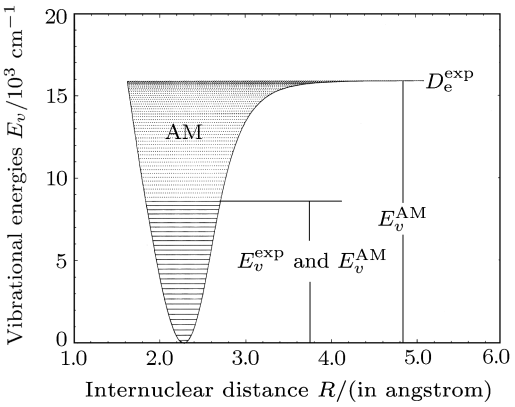


Fig. 1. vibrational energies $[E_\upsilon^{\rm exp}]$ and $\{E_\upsilon^{\rm AM}\}$ in the potential well of the $X^1\Sigma_{\rm g}^+$ state of Br_2 molecule. The experimental energies $[E_\upsilon^{\rm exp}]$ are from Ref. [16], and the $\{E_\upsilon^{\rm AM}\}$ is the full AM vibrational spectrum.

As we all know, it is usually very difficult to directly obtain molecular dissociation energy $D_{\rm e}$ or all accurate high-lying vibrational energies for most halogen diatomic electronic states by modern experimental techniques or quantum theories. However, those problems have been solved successfully in this work by AM and Eq. (23).

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