Rotational−Vibrational Levels of Diatomic Molecules Represented by the Tietz−Hua Rotating Oscillator

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Analytical expressions for the rotational−vibrational energy levels of diatomic molecules represented by the Tietz−Hua rotating oscillator are derived using the Hamilton−Jacoby theory and the Bohr−Sommerfeld quantization rule. In molecules with moderate and large values of rotational and vibrational quantum numbers, the levels are in much better agreement with the results of numerical calculations than the energies obtained from the common model of the rotating Morse oscillator.

1. Introduction

Atom−molecule and molecule−molecule collisions with transfer of molecular rotational and vibrational energy are important in plasma and material processing, supersonic and hypersonic flows, light sources, etc. Probabilities of the transitions depend on the molecular rotational−vibrational levels, and the transitions involving moderately and highly excited levels are often as important in gas kinetics as those involving weakly excited levels.[1] Therefore, a general and analytical expression for the molecular energies, accurate in a broad range of rotational and vibrational quantum numbers, is of a common interest in physics of high-temperature gas. Such expression would allow a substantial simplification of derivations of the transition probabilities for large number of atom−molecule and molecule−molecule collision systems and for quick and "transparent" evaluation of the main features of the collisions before they are incorporated into complex and time-consuming collisional-radiative models of high-temperature gas. Generality of the expression can be of great advantage in comparative studies of the molecular transitions in gases where many different collision systems simultaneously influence the gas properties.

The main goal of this work is to derive analytical expressions for molecular (diatomic) rotational−vibrational energy levels that have accuracy acceptable in applications and better than the accuracy of the commonly used expressions for the levels. We pay special attention to the reliability of the obtained expressions for moderate and high rotational−vibrational levels because these levels often play crucial role in the gas rotational−vibrational and dissociative kinetics.

General and analytical model potentials for diatomic molecules are available in literature (see ref 2 and references therein), and the potential most common in applications is the internuclear potential of the rotating Morse oscillator

$$V_{\mathrm{ef}}^{\mathrm{M}} = \frac{L^2}{2\mu R^2} + D[1 - \mathrm{e}^{-\beta(R-R_{\mathrm{e}})}]^2 \qquad (1)$$

where R is the internuclear distance, R_{e} is the molecular bond length, β is the Morse constant, D is the potential well depth, μ is the reduced mass of the oscillator, and L is its orbital angular momentum. The rotational−vibrational levels resulting from a simplified solution of the Schrödinger equation for the rotating Morse oscillator can be given as

$$E_{v,J}^{\mathrm{M}} = \omega_{\mathrm{e}}\left(v + \frac{1}{2}\right) - \omega_{\mathrm{e}}x_{\mathrm{e}}\left(v + \frac{1}{2}\right)^2 + B_{\mathrm{e}}J(1+J) - D_{\mathrm{e}}J^2(1+J)^2 \qquad (2)$$

where ω_{e}, $\omega_{\mathrm{e}}x_{\mathrm{e}}$, B_{e}, and D_{e} are the usual spectroscopic constants, and J and v are the molecular rotational and vibrational quantum numbers, respectively. Expression 2 is a truncated series expansion solution of the Schrödinger equation for the rotating Morse oscillator.[3] Even though more accurate (higher-order) expansions of the solution have been discussed in literature, eq 2 is the most common in applications (that is why we compare below this expression (instead of a higher-order expansion) with the results of the present work). The popularity of eq 2 results from the fact that the expression is simple and it predicts quite accurate values of the weakly-excited rotational−vibrational levels of diatomic molecules and that reliable values of the molecular spectroscopic constants ω_{e} and $\omega_{\mathrm{e}}x_{\mathrm{e}}$ are available in literature (most of the other constants in the higher-order expansion representing the rotational−vibrational energies of the Morse oscillator are not available in literature, and calculation of their accurate values is not trivial).

In molecules with moderate and high values of the rotational and vibrational quantum numbers, eq 2 is inaccurate. Therefore, we derive below a general and analytical expression for rotational−vibrational levels of diatomic molecules, which has accuracy acceptable in applications and better than the accuracy of eq 2. In order to do so, we use internuclear potential in which the rotational energy is the centrifugal energy of the molecular rotation (as it is done in relationship 1) and the vibrational energy is given by the function suggested by Tietz[4,5] and discussed in great detail by Hua;[6] this function (called hereafter the Tietz−Hua potential) reduces to, respectively, the Rosen−Morse,[7] Morse,[8] and Manning−Rosen[9] potentials for negative, zero, and positive values of the potential parameter c_{h} (this parameter is denoted by c in ref 6).

2. The Tietz−Hua Potential Function

If a diatomic molecule is represented by a rotating Tietz−Hua oscillator, then the internuclear potential of the molecule

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TABLE 1: Spectroscopic Constants and Other Parameters of the Diatomic Molecules Studied in the Present Work[a]

molecule	$HF(X^1\Sigma^+)$	$Cl_2(X^1\Sigma_g^+)$	$I_2(X\ (0_g^+))$	$H_2(X^1\Sigma_g^+)$	$O_2(X^3\Sigma_g^-)$
v_{max}	28	62	96	22	52
J_{max}	66	395	840	39	220
v_{max}^{M}	23	104	174	18	65
D	49382	20276	12547	38318	42041
$\mu/10^{-23}$	0.160	2.924	10.612	0.084	1.337
b_h	1.94207	2.20354	2.12343	1.61890	2.59103
y_e	1.78049	4.37843	5.66106	1.20032	3.12872
$w_e x_e$	89.88	2.67	0.61	121.33	11.98
B_e	20.956	0.244	0.037	60.853	1.438
D_e	0.0021	1.852×10^{-7}	4.537×10^{-9}	0.0465	4.760×10^{-6}
ω_e	4138.3	559.7	214.5	4401.2	1580.2
R_e	0.917	1.987	2.666	0.741	1.207
β	2.2266	2.0087	1.8643	1.9506	2.6636
ΔU_{TH}	0.0196	0.0189	0.0138	0.0265	0.0318
ΔU_{M}	0.0448	0.0606	0.0803	0.0576	0.0345
E_{max}/D	0.9928	0.9995	0.9997	0.9922	0.9999

[a] v_{max} and J_{max} are the maximum vibrational quantum number and the maximum rotational quantum number, respectively, for the rotating Tietz−Hua oscillator; v_{max}^{M} is the maximum vibrational quantum number for the Morse oscillator; c_h is the parameter in the potential 3; D is the well depth of the intramolecular potential (in cm^{-1}); μ is the reduced mass of the molecule (in g); b_h is the constant in the Tietz−Hua function (in Å^{-1}); $y_e = b_h R_e$, $\omega_e x_e$ is the anharmonicity constant (in cm^{-1}); B_e and D_e are the rotational constants (in cm^{-1}); ω_e is the vibrational constant (in cm^{-1}); R_e is the molecular bond length (in Å); β is the Morse constant (in Å^{-1}); $\Delta U_i = \overline{|U_i - U|}/D$ is the average deviation of the potential U_i from the corresponding "exact" potential U, where the U_i is the Tietz−Hua potential (the subscript TH) or the Morse potential (the subscript M), and U is the potential obtained either from the RKR (ref 6 and references therein) or from the *ab initio* calculations (ref 10 and references therein); E_{max} is the highest molecular energy assumed in the calculations of the parameter c_h.

can be given as

$$V_{ef}^{TH} = \frac{L^2}{2\mu R^2} + U_{TH} \tag{3}$$

where the first term on the right-hand side is the rotational (centrifugal) energy of the oscillator, and the second term is the vibrational energy (the Tietz−Hua potential) of the Tietz−Hua oscillator

$$U_{TH} = D\left[\frac{1 - e^{-b_h(R-R_e)}}{1 - c_h e^{-b_h(R-R_e)}}\right]^2 \tag{4}$$

with

$$b_h = \beta(1 - c_h) \tag{5}$$

where R is the internuclear distance, R_e is the molecular bond length, β is the Morse constant, D is the potential well depth, and c_h is the potential constant discussed below.

The reason for choosing the Tietz−Hua potential in this work is its remarkably good agreement (within a broad range of the internuclear distance) with the RKR (Rydberg−Klein−Rees) (ref 6 and references therein) and *ab initio* calculations (ref 10 and references therein); see also discussions in refs 11 and 5. According to these works, the Tietz−Hua potential is much more realistic than the Morse potential in description of molecular dynamics at moderate and high rotational and vibrational quantum numbers. Also, it was shown in refs 5 and 12 that all practically significant analytical potentials allowing solution of the one-dimensional Schrödinger equation in terms of hypergeometric functions (the Tietz−Hua potential belongs to this category) have been already reported in the literature and that it is practically impossible to discover a new potential of this kind. Thus, the Tietz−Hua potential seems to be one of the very best analytical model potentials for the vibrational energy of diatomic molecules. Therefore, we use it in the relationship 3, which is our choice of analytical approximation to the "exact" potentials (obtained from the RKR and *ab initio* calculations) in diatomic molecules. Consequently, one of the main tasks of this work is to obtain accurate values of the parameters c_h from the exact potentials.

The parameter c_h of the Tietz−Hua potential is obtained here, like in ref 6, from minimalization of the average value of the ratio $\Delta U_i = |U_i - U|/D$, where the internuclear potential U_i is obtained from the Tietz−Hua function, and U is the exact potential obtained from either RKR or *ab initio* calculations (the average is taken over all available data points of the exact potential). Thus, the degree of the overall agreement between the exact potentials and the potentials 1 and 3 is measured here by the ratios ΔU_i (see Tables 1 and 2; the corresponding values of c_h are given in Table 3). The ratios are much smaller than 1 (typically, they are smaller than 0.05). However, one should emphasize that a small value of such a ratio does not automatically mean that the shapes of the compared potential curves are equally close to one another in the entire considered range of the internuclear distance R. Thus, for example, potential 1 and potential 3 for some molecules may have very similar values of ΔU_i, but the potential curves does not have to overlap in most of the range of the distance R. This lack of the overlapping can produce two (one for each of the compared potentials) substantially different sets of the rotational−vibrational levels even though the values of ΔU_i for the both curves are very similar.

Choice of the Morse constant β is not a simple issue. Solution of the Schrödinger equation for the Morse potential gives the following vibrational constants

$$\omega_e = \beta\left[\frac{D}{2\pi^2 c^2 \mu}\right]^{1/2} \tag{6}$$

and

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu} \tag{7}$$

where ω_e and $\omega_e x_e$ are in cm^{-1}, D is in ergs, and the rest of the quantities are in units of the cgs system. Thus, the constant β obtained from the expression 6 will differ from that resulting from the expression 7 if the spectroscopic constants ω_e, $\omega_e x_e$, and D are taken as the "best available" in literature; the latter

TABLE 2: Spectroscopic Constants and Other Parameters of the Diatomic Molecules Studied in the Present Work[a]

molecule	$N_2(X^1\Sigma_g^+)$	$NO(X^2\Pi_r)$	$O_2^+(X^2\Pi_g)$	$N_2^+(X^2\Sigma_g^+)$	$NO^+(X^1\Sigma^+)$
v_{max}	66	56	56	62	72
J_{max}	260	230	235	250	270
v_{max}^M	82	67	58	68	73
D	79885	53341	54688	71365	88694
$\mu/10^{-23}$	1.171	1.249	1.337	1.171	1.239
b_h	2.78585	2.71559	2.86987	2.70830	2.73349
y_e	3.05797	3.12502	3.20392	3.02360	2.90630
w_ex_e	14.32	14.07	16.25	16.10	16.26
B_e	1.998	1.672	1.691	1.932	1.997
D_e	5.737×10^{-6}	5.156×10^{-6}	5.334×10^{-6}	5.920×10^{-6}	5.643×10^{-6}
ω_e	2358.6	1904.2	1904.8	2207.0	2376.4
R_e	1.097	1.151	1.116	1.116	1.063
β	2.6986	2.7534	2.8151	2.6717	2.6552
ΔU_{TH}	0.0349	0.0619	0.0176	0.0287	0.0169
ΔU_M	0.0440	0.0722	0.0204	0.0301	0.0226
E_{max}/D	0.9999	0.9999	0.9999	0.9999	0.9999

[a] Meaning of the symbols is the same as in Table 1.

TABLE 3: Coefficients c_h, ω_0, ω_1 in Expressions 43 and 44

molecule	c_h	ω_0	ω_1
$HF(X^1\Sigma^+)$	0.127 772	0.004 669 77	−0.000 063 53
$Cl_2(X^1\Sigma_g^+)$	−0.096 988	−0.001 468 49	0.000 013 27
$I_2(X\ (O_g^+))$	−0.139 013	−0.001 353 47	$8.420\,80 \times 10^{-6}$
$H_2(X^1\Sigma_g^+)$	0.170 066	0.008 106 09	−0.000 012 75
$O_2(X^3\Sigma_g^-)$	0.027 262	0.000 498 39	$-4.307\,26 \times 10^{-6}$
$N_2(X^1\Sigma_g^+)$	−0.032 325	−0.000 492 60	$3.996\,40 \times 10^{-6}$
$NO(X^2\Pi_r)$	0.013 727	0.000 241 66	$-2.068\,81 \times 10^{-6}$
$O_2^+(X^2\Pi_g)$	−0.019 445	−0.000 345 22	$3.183\,68 \times 10^{-6}$
$N_2^+(X^2\Sigma_g^+)$	−0.013 716	−0.000 215 00	$1.731\,34 \times 10^{-6}$
$NO^+(X^1\Sigma^+)$	−0.029 477	−0.000 406 55	$2.968\,89 \times 10^{-6}$

constants are not consistent with the model of the Morse oscillator because they are usually obtained from measurements and *ab initio* calculations. (The expressions 6 and 7 give the same values of β only when the Birge−Sponer relationship, $D = \omega_e^2/4\omega_ex_e$, is applied. However, the Birge−Sponer approximation can lead to errors in values of D that can be as large as 30%).

In this work, we calculate β from the relationship 6 (Tables 1 and 2) because the constants ω_e and D available in literature are usually more accurate than the anharmonicity constants ω_ex_e (also, expression 6 is identical with the corresponding expression obtained from comparison of the vibrational force constants for harmonic and Morse oscillators at $R = R_e$).

The anharmonicity constants ω_ex_e used in the present calculations are those obtained from the "best available" data (typically, these constants differ from those predicted by expression 7 if β is obtained from expression 6). The reason for this choice of ω_ex_e is the fact that all the "exact" (RKR and *ab initio*) calculations of the internuclear potentials discussed in this work used the "best available" values of the anharmonicity constants.

3. The Rotational−Vibrational Energy Levels

Using the Hamilton−Jacoby theory and the Bohr−Sommerfeld quantization rule, Porter *et al.*[13] studied, using the model of the rotating Morse oscillator, the rotational−vibrational dynamics of diatomic molecules. In this paper, we apply their semiclassical approach to diatomic molecules with intramolecular potential given by relationship 3. Subsequently, the Hamiltonian of the rotating Tietz−Hua oscillator with angular momentum L can be written as

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu R^2} + D\left[\frac{1 - e^{-b_h(R-R_e)}}{1 - c_h e^{-b_h(R-R_e)}}\right]^2 \tag{8}$$

where $p_r = \mu(dR/dt)$ is the oscillator linear momentum.

The equilibrium internuclear distance R_* of a molecule in the Jth rotational level can be obtained from the derivative

$$\frac{dV_{ef}(R)}{dR} = 0 \tag{9}$$

which, after introducing a new variable

$$C_J = \frac{b_h^2 L^2}{2\mu D} \tag{10}$$

becomes

$$\frac{dV_{ef}(R)}{dR} = \left[\frac{1 - e^{-y_*}e^{y_e}}{(1 - c_h e^{-y_*}e^{y_e})^3}\right](1 - c_h) - e^{y_*}e^{-y_e}\frac{C_J}{y_*^3} = 0 \tag{11}$$

where

$$y_* = b_hR_* \quad \text{and} \quad y_e = b_hR_e \tag{12}$$

When $J \rightarrow 0$, $C_J \rightarrow 0$, eq 11 can be written

$$\left[\frac{1 - e^{-y_*}e^{y_e}}{(1 - c_h e^{-y_*}e^{y_e})^3}\right](1 - c_h) = 0 \rightarrow 1 = e^{-y_*+y_e} \quad \text{and} \quad y_* = y_e \tag{13}$$

which suggests the possibility of an asymptotic solution of the transcendental equation 11 which depends on a small parameter (c_h). Such a solution can be obtained as an asymptotic expansion in terms of this small parameter.[14] We propose the following expansion

$$y_* = y_e + B_hC_J + D_hC_J^2 \tag{14}$$

where the values of the coefficients B_h and D_h can be obtained by substituting eq 14 into eq 11 and using the fact that $C_J(J{\rightarrow}0) \rightarrow 0$. (Note that expression 14 is also valid for the Morse oscillator when $c_h = 0$.) As a result, one has

$$\frac{e^{-B_hC_J-D_hC_J^2} - e^{-2B_hC_J-2D_hC_J^2}}{(1 - c_h e^{-B_hC_J-D_hC_J^2})^3}(1 - c_h) = \frac{C_J}{(y_e + B_hC_J + D_hC_J^2)^3} \tag{15}$$

Since $C_J(J{\rightarrow}0) \rightarrow 0$, we can use the expansion of $e^x \simeq 1 + x + x^2/2 + ...$ and limit the expression for the cubic function

$(y_e + B_h C_J + D_h C_J^2)^3$ to linear and quadratic terms of C_J. After some algebra, one obtains

$$[B_h C_J + D_h C_J^2 - (3/2)B_h^2 C_J^2](y_e^3 + 3y_e^2 B_h C_J + 3y_e B_h^2 C_J^2 + 3y_e^2 D_h C_J^2)(1 - c_h) = C_J[1 + 3c_h(B_h C_J + D_h C_J^2 - (1/2)B_h^2 C_J^2 - 1) + 3c_h^2(2B_h^2 C_J^2 - 2B_h C_J - 2D_h C_J^2 + 1) + 3c_h^3(D_h C_J^2 - (3/2)B_h^2 C_J^2 + B_h C_J - (1/3))] \quad (16)$$

where comparison of the coefficients in the terms with the same powers of C_J gives

$$B_h = \frac{(1 - c_h)^2}{y_e^3} \quad \text{and} \quad D_h = \frac{3}{2}B_h^2 - 3\frac{B_h^2}{y_e} + \frac{3B_h c_h(1 - c_h)}{y_e^3} \quad (17)$$

The ratio y_*/y_{*n} ($y_{*n} = b_h R_{*n}$, where R_{*n} is the numerical solution of eq 11) for diatomic molecules is increasing with increase of the rotational quantum number J. The values of the ratio are usually not greater than about 1.03, except for the $H_2(X^1\Sigma_g^+)$ and $HF(X^1\Sigma^+)$ molecules where the ratio at $J \approx J_{max}$ is about 1.05 (J_{max} is the maximum value of the molecular rotational quantum number).

Using the above we calculated the values of the ratios ΔU_i and E_{max}/D (E_{max} is the maximum value of the molecular energy taken into account in the *ab initio* and RKR calculations used in this work) for several diatomic molecules (see Tables 1 and 2).

In order to apply the approach of ref 13, we introduce a new variable, $\xi_*(R) = \exp(-b_h(R - R_*))$, and use the following series expansion of $1/(b_h R)^2$ about $\xi_* = 1$

$$\frac{1}{(b_h R)^2} = \frac{1}{(b_h R_*)^2} + \frac{2}{(b_h R_*)^3}(\xi_* - 1) - \frac{1}{(b_h R_*)^3}\left(1 - \frac{3}{b_h R_*}\right)(\xi_* - 1)^2 + ... \quad (18)$$

where R_*, the internuclear distance corresponding to the minimum of the intramolecular potential of the molecule with $J > 0$, is given by the relationships 12 and 14.

Substituting the expansion 18 into eq 8 and solving for p_r (the radial momentum of the vibrating molecule) at fixed value of the rotational−vibrational energy $H = E_{v,J}$ gives

$$p_r = \pm(2\mu)^{1/2} \times \left[E_{v,J} - L^2(A_* + B_*\xi_* - C_*\xi_*^2) - D\left(\frac{1 - \xi_*\xi_{e*}}{1 - c_h\xi_*\xi_{e*}}\right)^2\right]^{1/2} \quad (19)$$

where

$$\xi_{e*} = e^{-b_h(R_* - R_e)} \quad (20)$$

$$L^2 = \hbar^2[J(J + 1) - \Lambda^2] \quad (21)$$

where Λ is the quantum number for the axial component of the molecular electronic angular momentum, and the coefficients A_*, B_*, and C_* are

$$A_* = \left[1 + \frac{3}{b_h R_*(b_h R_* - 3)}\right] b_h R_* C_* \quad (22)$$

$$B_* = 2\left[1 + \frac{b_h R_*}{(b_h R_* - 3)}\right] C_* \quad (23)$$

and

$$C_* = \frac{1}{2\mu b_h R_*^3}\left(1 - \frac{3}{b_h R_*}\right) \quad (24)$$

The energy of the rotating Tietz−Hua oscillator is calculated below using the Bohr−Sommerfeld quantization rule

$$N_v = \frac{1}{2\pi}\oint p_r \, dr = \left(v + \frac{1}{2}\right)\hbar \quad (25)$$

where v is the vibrational quantum number. As shown in the Appendix, the quantization rule leads to the following expression for the rotational−vibrational levels of the diatomic molecules

$$E'_{v,J} = D + L^2(A_* - 3u^2 C_* - u^2 B_* - 2uC_*) - \left[(v + {}^1/_2)\frac{\hbar b_h}{(2\mu)^{1/2}} - F'_1 - F'_2 L^2 - F'_3 L^4\right]^2 \quad (26)$$

where μ is the reduced mass of the molecule, $u = c_h\xi_{e*}$ and

$$F'_1 = \frac{k_1 - 4\xi_{e*}D\mu}{-4\mu\xi_{e*}D^{1/2} + k_2} \quad (27)$$

$$F'_2 = \frac{-2\mu}{-4\mu\xi_{e*}D^{1/2} + k_2}\left[\varphi'_2 + F'_1\frac{\varphi'_1}{\xi_{e*}D^{1/2}}\right] \quad (28)$$

$$F'_3 = \frac{-\mu\varphi'_1}{\xi_{e*}D^{1/2}(-4\mu\xi_{e*}D^{1/2} + k_2)}\left[2F'_2 + F'_1\frac{\varphi'_1}{2\xi_{e*}^2 D}\right] \quad (29)$$

$$\varphi'_1 = 6u^2 C_* + 3u^2 B_* + 6uC_* + 2uB_* + C_* \quad (30)$$

$$\varphi'_2 = -(8u^2 C_* + 3u^2 B_* + 6uC_* + B_*) \quad (31)$$

$$k_1 = u\hbar^2(v + {}^1/_2)^2 b_h^2 \quad (32)$$

$$k_2 = 2u\hbar(v + {}^1/_2)b_h(2\mu)^{1/2} \quad (33)$$

The values of the energy levels obtained from expression 26 are in very good agreement (with accuracy better than 1%) for all molecules considered here (except the $H_2(X^1\Sigma_g^+)$ molecule—see discussion below) and in the entire range of vibrational, $0 \leq v \leq v_{max}$ (v_{max} is the maximum vibrational quantum number of the rotationless molecule), and rotational, $0 \leq J \leq J_{max}$, quantum numbers, with the corresponding energy values obtained from numerical solution of the Schrödinger equation[15] for the potential 3.

Numerical calculations show that the dependence of the functions F'_2 and F'_3 on v is weak for all values of v between 0 and v_{max}. Therefore, assuming in F'_2 and F'_3 that $v = v_{max}/2$, one obtains another expression for the rotational-vibrational energies of diatomic molecules

$$E''_{v,J} = D + L^2 B_J B''_J - (F_0 x_1 - F''_1 - F'''_2 L^2 - F'''_3 L^4)^2 \quad (34)$$

where

$$B_J = \frac{\omega_2}{(b_h R_*)^4} \quad (35)$$

$$B''_J = (b_h R_*)^2 - b_h R_*(7u^2 + 2u + 3) + 15u^2 + 6u + 3 \quad (36)$$

$$F_0 = \frac{\hbar b_h}{\sqrt{2\mu}} \tag{37}$$

$$F_1'' = \sqrt{D}(1 + \omega_0 x_1 + \omega_1 x_1^2) \tag{38}$$

$$F_2''' = A_J(1 + \omega_0 x_2 + \omega_0^2 x_2^2)\left(-\eta_{1J} + \frac{\eta_{2J}}{\xi_{e*}\sqrt{D}}\sqrt{D}(1 + \omega_0 x_2 + \omega_1 x_2^2)\right) \tag{39}$$

$$F_3''' = \frac{A_J \eta_{2J}}{\xi_{e*}\sqrt{D}}(1 + \omega_0 x_2 + \omega_0^2 x_2^2) \times \left(F_2''' + \frac{A_J \eta_{2J}}{2\xi_{e*}\sqrt{D}}\sqrt{D}(1 + \omega_0 x_2 + \omega_1 x_2^2)\right) \tag{40}$$

$$x_1 = v + 1/2 \tag{41}$$

$$x_2 = (v_{\max}^{\mathrm{TH}} + 1)/2 \tag{42}$$

$$\omega_0 = \frac{\hbar b_h c_h}{\sqrt{2\mu D}} \tag{43}$$

$$\omega_1 = \omega_0^2\left(1 - \frac{1}{2c_h}\right) \tag{44}$$

$$A_J = \frac{\omega_2}{2\sqrt{D}\xi_{e*}(b_h R_*)^4} \tag{45}$$

$$\omega_2 = \frac{b_h^2}{2\mu} \tag{46}$$

$$\eta_{1J} = b_h R_*(20u^2 + 6u + 4) - (42u^2 + 18u + 6) \tag{47}$$

and

$$\eta_{2J} = b_h R_*(18u^2 + 14u + 1) - (36u^2 + 30u + 3) \tag{48}$$

and the maximum value of the vibrational quantum number in the Tietz−Hua oscillator is (see Appendix)

$$v_{\max}^{\mathrm{TH}} = \frac{1 - c_h - (1 - 3c_h^2)^{1/2}}{\omega_0(2c_h - 1)} - \frac{1}{2} \tag{49}$$

One should mention that the maximum vibrational quantum number $v_{\max}^{\mathrm{M}}$ of the Morse oscillator, obtained from the function 2, can be taken as the integer closest to, and smaller than

$$v_{\max}^{\mathrm{M}} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \tag{50}$$

In order to evaluate the accuracy of the expression 34, we calculated the energies $E''_{v,J}$ of 10 diatomic molecules and molecular ions representing a broad range of spectroscopic constants (Tables 1 and 2). The results for two of the molecules ($N_2(X^1\Sigma_g^+)$ and $H_2(X^1\Sigma_g^+)$) are shown in Figures 1 and 2, together with the rotational-vibrational eigenvalues obtained from numerical solution of the Schrödinger equation for the potential 3 and with the energies predicted by eq 2. (The accuracy of the expression 34 for the $N_2(X^1\Sigma_g^+)$ molecule is very close to the accuracies of the expression for all, except $H_2(X^1\Sigma_g^+)$ and $HF(X^1\Sigma^+)$, molecules listed in Tables 1 and 2).

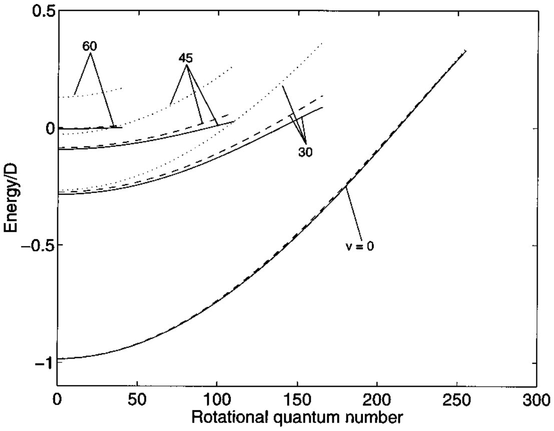

Figure 1. Rotational−vibrational energies $E''_{v,J}$ (dashed line, eq 34) and $E^{\mathrm{M}}_{v,J}$ (dotted line, eq 2) and the energy obtained from numerical solution of the Schrödinger equation for the potential 3 (solid line) for the $N_2(X^1\Sigma_g^+)$ molecule. The zero rotational−vibrational energy corresponds to the dissociation continuum of the rotationless molecule. v and J are vibrational and rotational quantum numbers, respectively.

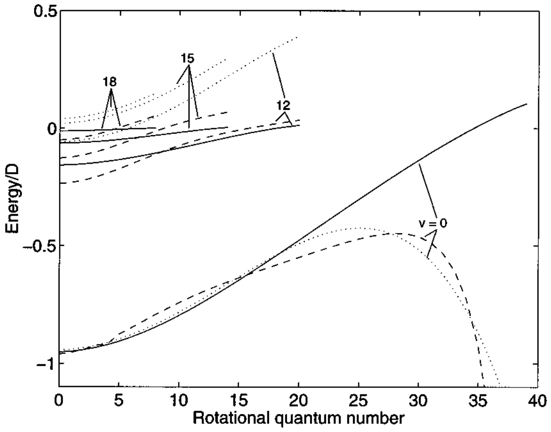

Figure 2. Rotational−vibrational energies $E''_{v,J}$ (dashed line) and $E^{\mathrm{M}}_{v,J}$ (dotted line) and the energy obtained from numerical solution of the Schrödinger equation for the potential 3 (solid line) for the H_2 $(X^1\Sigma_g^+)$ molecule. Meaning of the symbols is the same as in Figure 1.

As can be seen in Figures 1 and 2, expression 34 is always more accurate in describing the rotational−vibrational levels of diatomic molecules than relationship 2. (The accuracy of the Morse model increases with decrease of the degree of the rotational−vibrational excitation of the molecules, while the agreement of the relationship 34 with the numerical solution of the Schrödinger equation for the potential 3 is quite good in the entire range of the vibrational and rotational quantum numbers.) Expression 34 is less accurate for low v in the case of the $H_2(X^1\Sigma_g^+)$ and $HF(X^1\Sigma^+)$ molecules (the accuracies of the expression for these two molecules are similar). Therefore, it is more accurate to use in such cases the expression 26 with the sum $F_1' - F_2'L^2 - F_3'L^4$ being replaced by the exact expression 65 (see Appendix and Figure 3).

One should notice the significant differences between the values of $v_{\max}$ obtained in the present work and those resulting from the model of the Morse oscillator (Tables 1 and 2). The difference can be as big as the one in the $I_2(X(0_g^+))$ molecule where $v_{\max} = 96$ (the present model) and 174 (the Morse model). This is a clear failure of the Morse model because the realistic value of $v_{\max}$ in the $I_2(X(0_g^+))$ molecule is about 107 (see ref 16).

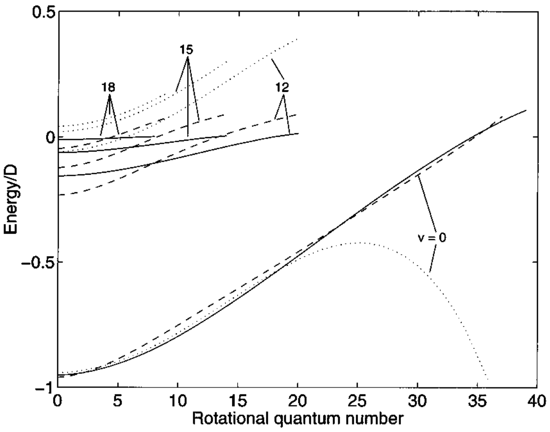

Figure 3. Rotational−vibrational energies $E'_{v,J}$ (dashed line, eq 26 with the sum $F'_1 - F'_2L^2 - F'_3L^4$ being replaced by the exact expression 65), and $E^{\mathrm{M}}_{v,J}$ (dotted line) and the energy obtained from numerical solution of the Schrödinger equation for the potential 3 (solid line) for the $\mathrm{H_2(X^1\Sigma_g^+)}$ molecule. Meaning of the symbols is the same as in Figure 1.

4. Summary

Summarizing the above, one can say that relationship 34 is a good analytical approximation to the rotational−vibrational levels of diatomic molecules (including molecular ions) in the ground electronic states. The relationship should also be able to predict reasonable values of the rotational−vibrational levels of the electronically excited diatomic molecules that can be treated as the rotating Tietz−Hua oscillators.

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Appendix

In this Appendix we summarize the mathematical transformations leading to the expressions 26 and 34 for the rotational−vibrational energies of diatomic molecules, according to the model of the rotating Tietz−Hua oscillator.

Changing the variable r in eq 19 to ξ_* one has

$$N_v = -\frac{(2\mu)^{1/2}}{\pi b_{\mathrm{h}}}\int_{\xi_{*<}}^{\xi_{*>}} \{[E_{v,J} - L^2(A_* + B_*\xi_* - C_*\xi_*^2)] \times (1 - c_{\mathrm{h}}\xi_*\xi_{\mathrm{e}*})^2 - D(1 - \xi_*\xi_{\mathrm{e}*})^2\}^{1/2}/[\xi_*(1 - c_{\mathrm{h}}\xi_*\xi_{\mathrm{e}*})]\,\mathrm{d}\xi_* \tag{51}$$

where $\xi_{*<}$ and $\xi_{*>}$ are roots of equation $p_{\mathrm{r}} = 0$. To obtain the roots, we first rearrange the terms in eq 19 so that the equation can be written as the following fourth-order polynomial

$$f_1(\xi_*) = a_{\mathrm{f}}\xi_*^4 + b_{\mathrm{f}}\xi_*^3 + c_{\mathrm{f}}\xi_*^2 + d_{\mathrm{f}}\xi_* + e_{\mathrm{f}} = 0 \tag{52}$$

with

$$a_{\mathrm{f}} = c_{\mathrm{h}}^2\xi_{\mathrm{e}*}^2C_*L^2 \tag{53}$$

$$b_{\mathrm{f}} = B_*L^2c_{\mathrm{h}}^2\xi_{\mathrm{e}*}^2 + 2c_{\mathrm{h}}\xi_{\mathrm{e}*}C_*L^2 \tag{54}$$

$$c_{\mathrm{f}} = c_{\mathrm{h}}^2\xi_{\mathrm{e}*}^2(E_{v,J} - A_*L^2) + 2B_*L^2c_{\mathrm{h}}\xi_{\mathrm{e}*} + C_*L^2 - \xi_{\mathrm{e}*}^2D \simeq 2B_*L^2c_{\mathrm{h}}\xi_{\mathrm{e}*} + C_*L^2 - \xi_{\mathrm{e}*}^2D \tag{55}$$

$$d_{\mathrm{f}} = 2\xi_{\mathrm{e}*}D - B_*L^2 - 2c_{\mathrm{h}}\xi_{\mathrm{e}*}(E_{v,J} - A_*L^2) \simeq 2\xi_{\mathrm{e}*}D - B_*L^2 \tag{56}$$

and

$$e_{\mathrm{f}} = E_{v,J} - A_*L^2 - D \tag{57}$$

where the simplification of the coefficients c_{f} and d_{f} resulted from the fact that c_{h} is a small parameter.

Let us now expand $f_1(\xi_*)$ in power series about $\xi_* = 1$ retaining only terms which are linear or quadratic in ξ_*

$$f_1(\xi_*) \simeq f_2(\xi_*) = \varphi_1\xi_*^2 + \varphi_2\xi_* + \varphi_3 \tag{58}$$

where

$$\varphi_1 = 6a_{\mathrm{f}} + 3b_{\mathrm{f}} + c_{\mathrm{f}},\quad \varphi_2 = -8a_{\mathrm{f}} - 3b_{\mathrm{f}} + d_{\mathrm{f}},\quad \varphi_3 = 3a_{\mathrm{f}} + b_{\mathrm{f}} + e_{\mathrm{f}} \tag{59}$$

This allows one to evaluate the integral 51 as follows

$$-\frac{(2\mu)^{1/2}}{\pi b_{\mathrm{h}}}\int_{\xi_{*<}}^{\xi_{*>}}\frac{\sqrt{f_1}}{\xi_*(1 - u\xi_*)}\,\mathrm{d}\xi_* \simeq -\frac{(2\mu)^{1/2}}{\pi b_{\mathrm{h}}}\int_{\xi_{*<}}^{\xi_{*>}}\frac{\sqrt{f_2}}{\xi_*(1 - u\xi_*)}\,\mathrm{d}\xi_* \tag{60}$$

($u = c_{\mathrm{h}}\xi_{\mathrm{e}*}$, and $\xi_{*<}$ and $\xi_{*>}$ are now the roots of equation $f_2(\xi_*) = 0$), which leads to

$$-\frac{(2\mu)^{1/2}}{\pi b_{\mathrm{h}}}\int_{\xi_{*<}}^{\xi_{*>}}\frac{\sqrt{f_2}}{\xi_*(1 - u\xi_*)}\,\mathrm{d}\xi_* = -\frac{(2\mu)^{1/2}}{\pi b_{\mathrm{h}}}[(-\sqrt{-\varphi_1} + \sqrt{-\varphi_3u^2}) + \sqrt{-\varphi_1 - \varphi_2u - \varphi_3u^2}] \tag{61}$$

where the limits of integration are

$$\xi_{*>} = \frac{-\varphi_2 - \sqrt{\varphi_2^2 - 4\varphi_1\varphi_3}}{2\varphi_1} \quad\text{and}\quad \xi_{*<} = \frac{-\varphi_2 + \sqrt{\varphi_2^2 - 4\varphi_1\varphi_3}}{2\varphi_1} \tag{62}$$

The relationship 51 can now be written as

$$N_v = -(-\sqrt{-\varphi_1} + \sqrt{-\varphi_3u^2}) - \sqrt{-\varphi_1 - \varphi_2u - \varphi_3u^2} = \frac{\hbar(v + {}^1\!/_2)ub_{\mathrm{h}}}{(2\mu)^{1/2}} \tag{63}$$

and, after some algebra

$$-\sqrt{-\varphi_3} = \frac{\hbar(v + {}^1\!/_2)b_{\mathrm{h}}}{(2\mu)^{1/2}} - \frac{u\hbar^2(v + {}^1\!/_2)^2b_{\mathrm{h}}^2 - 2\mu\varphi_2}{-4\mu\sqrt{-\varphi_1} + 2u\hbar(v + {}^1\!/_2)b_{\mathrm{h}}(2\mu)^{1/2}} \tag{64}$$

Let us denote the last term in eq 64 by $F_{v,J}$

$$F_{v,J} = \frac{k_1 - 2\mu\varphi_2}{-4\mu\sqrt{-\varphi_1} + k_2} \tag{65}$$

($k_1 = u\hbar^2(v + {}^1/_2)^2 b_h^2$ and $k_2 = 2u\hbar(v + {}^1/_2)b_h(2\mu)^{1/2}$) and expand it with respect to L^2. The resulting expression is

$$F_{v,J} \simeq F'_1 + F'_2 L^2 + F'_3 L^4 + ... \tag{66}$$

where

$$F'_1 = \frac{k_1 - 4\xi_{e*}D\mu}{-4\mu\xi_{e*}D^{1/2} + k_2} \tag{67}$$

$$F'_2 = \frac{-2\mu}{-4\mu\xi_{e*}D^{1/2} + k_2}\left[\varphi'_2 + F'_1\frac{\varphi'_1}{\xi_{e*}D^{1/2}}\right] \tag{68}$$

and

$$F'_3 = \frac{-\mu\varphi'_1}{\xi_{e*}D^{1/2}(-4\mu\xi_{e*}D^{1/2} + k_2)}\left[2F'_2 + F'_1\frac{\varphi'_1}{2\xi_{e*}^2 D}\right] \tag{69}$$

with

$$\varphi'_1 = \partial\varphi_1/\partial L^2 = 6u^2C_* + 3u^2B_* + 6uC_* + 2uB_* + C_* \tag{70}$$

and

$$\varphi'_2 = \partial\varphi_2/\partial L^2 = -(8u^2C_* + 3u^2B_* + 6uC_* + B_*) \tag{71}$$

Solving eq 64 for φ_3 and taking into account eqs 65−71, one obtains the expression 26 for the rotational−vibrational levels of the diatomic molecules

$$E'_{v,J} = D + L^2(A_* - 3u^2C_* - u^2B_* - 2uC_*) - \left[(v + {}^1/_2)\frac{\hbar b_h}{(2\mu)^{1/2}} - F'_1 - F'_2L^2 - F'_3L^4\right]^2 \tag{72}$$

Since in diatomic molecules

$$|c_h\sqrt{\frac{1}{2\mu D}}\hbar b_h(v + {}^1/_2)| \ll 1 \tag{73}$$

the eqs 67−69 can be approximated, respectively, by

$$F''_1 = \sqrt{D}(1 + \omega_0x_1 + \omega_1x_1^2) \tag{74}$$

$$F''_2 = A_J(1 + \omega_0x_1 + \omega_0^2x_1^2)\left(-\eta_{1J} + \frac{\eta_{2J}}{\xi_{e*}\sqrt{D}}F''_1\right) \tag{75}$$

and

$$F''_3 = \frac{A_J\eta_{2J}}{\xi_{e*}\sqrt{D}}(1 + \omega_0x_1 + \omega_0^2x_1^2)\left(F''_2 + \frac{A_J\eta_{2J}}{2\xi_{e*}\sqrt{D}}F''_1\right) \tag{76}$$

where

$$x_1 = (v + {}^1/_2) \tag{77}$$

$$\omega_0 = \frac{\hbar b_hc_h}{\sqrt{2\mu D}} \tag{78}$$

$$\omega_1 = \omega_0^2\left(1 - \frac{1}{2c_h}\right) \tag{79}$$

$$A_J = \frac{\omega_2}{2\sqrt{D}\xi_{e*}(b_hR_*)^4} \tag{80}$$

$$\omega_2 = \frac{b_h^2}{2\mu} \tag{81}$$

$$\eta_{1J} = b_hR_*(20u^2 + 6u + 4) - (42u^2 + 18u + 6) \tag{82}$$

and

$$\eta_{2J} = b_hR_*(18u^2 + 14u + 1) - (36u^2 + 30u + 3) \tag{83}$$

Numerical calculations show that the dependence of the functions F'_2 and F'_3 on v is weak for all values of v between 0 and v_{max} (v_{max} is the maximum vibrational quantum number of the rotationless molecule). Therefore, one can assume in relationships 75 and 76 that $v = v_{max}^{TH}/2$. In the case of the Tietz−Hua oscillator, the maximum vibrational quantum number v_{max}^{TH} can be obtained from the function 72 by replacing F'_1 by F''_1 (because of relationship 73),

$$\frac{dE'_{v,J=0}}{dx_1} = 0 \rightarrow -2(F_0x_1 - F''_1)\left(F_0 - \frac{dF''_1}{dx_1}\right) = 0 \tag{84}$$

with

$$F_0 = \frac{\hbar b_h}{\sqrt{2\mu}} \tag{85}$$

and

$$\frac{dF''_1}{dx_1} = \omega_0\sqrt{D} + 2\omega_1x_1\sqrt{D} \tag{86}$$

Numerical solution of eq 84 gives the maximum vibrational quantum number v_{max}^{TH} which is very close to the corresponding value obtained from analytical solution of the following equation

$$E'_{v,J=0} - D = 0 \tag{87}$$

This analytical solution, the smallest positive root of eq 87, is

$$v_{max}^{TH} = \frac{1 - c_h - (1 - 3c_h^2)^{1/2}}{\omega_0(2c_h - 1)} - \frac{1}{2} \tag{88}$$

Taking the above into account, the relationship 72 leads to the main expression 34 of this work for the rotational−vibrational energies of diatomic molecules

$$E''_{v,J} = D + L^2B_JB''_J - (F_0x_1 - F''_1 - F'''_2L^2 - F'''_3L^4)^2 \tag{89}$$

where

$$B_J = \frac{\omega_2}{(b_hR_*)^4} \tag{90}$$

$$B''_J = (b_hR_*)^2 - b_hR_*(7u^2 + 2u + 3) + 15u^2 + 6u + 3 \tag{91}$$

$$x_2 = (v_{max}^{TH} + 1)/2 \tag{92}$$

$$F_0 = \frac{\hbar b_\mathrm{h}}{\sqrt{2\mu}} \tag{93}$$

$$F_2''' = A_J(1 + \omega_0 x_2 + \omega_0^2 x_2^2) \times \left(-\eta_{1J} + \frac{\eta_{2J}}{\xi_{\mathrm{e}*}\sqrt{D}}\sqrt{D}(1 + \omega_0 x_2 + \omega_1 x_2^2)\right) \tag{94}$$

and

$$F_3''' = \frac{A_J \eta_{2J}}{\xi_{\mathrm{e}*}\sqrt{D}}(1 + \omega_0 x_2 + \omega_0^2 x_2^2) \times \left(F_2''' + \frac{A_J \eta_{2J}}{2\xi_{\mathrm{e}*}\sqrt{D}}\sqrt{D}(1 + \omega_0 x_2 + \omega_1 x_2^2)\right) \tag{95}$$

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