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High-Accuracy Expressions for Rotational–Vibrational Energies of O_2, N_2, NO, and CO Molecules

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Application of the Hamilton–Jacoby theory and the Bohr–Sommerfeld quantization rule to the rotating Morse oscillator yields analytical expressions for the rotational–vibrational energy levels of the O_2, N_2, NO, and CO molecules in electronic ground states. The expressions give more realistic values of the moderately and highly excited rotational–vibrational levels than the corresponding levels obtained from the common truncated expansion solution of the Schrödinger equation for the rotating Morse oscillator.

I. Introduction

PROPERTIES of rotationally and vibrationally excited diatomic molecules are of significant importance in studies of dissociation, chemical reactions, and rotation–vibration, vibration–vibration, and vibration–translation transitions in high-temperature gases in material and plasma processing, supersonic and hypersonic flows, light sources, and environmental studies. The properties depend on intramolecular potentials of the molecules, and many analytical expressions for the potentials have been proposed in literature (see Ref. 1, hereafter called Paper I, and references therein). One of the most accurate of these potentials for vibrating and rotating diatomic molecules is the potential resulting from superposition of the Tietz–Hua potential[2,3] (representing the vibrational part of the atom–atom interaction in the molecules) and the centrifugal stretching term representing the rotational part of the interaction. (The model of molecular rotational–vibrational motion driven by such intramolecular potential is called hereafter the rotating Tietz–Hua oscillator.) However, the most commonly used intramolecular potential is a superposition of the Morse potential and the molecular centrifugal energy; the corresponding model of diatomic molecule is called the rotating Morse oscillator. The popularity of the latter model results from the fact that its rotational–vibrational energies $E_{v,J}$ can be given as a series expansion, and that the truncated form of the expansion [given in Eq. (2)] is very simple.[4] However, it is well known (see discussion in Paper I) that the truncated expansion has poor accuracy at moderate and high vibrational and rotational quantum numbers.

In Paper I we applied the Hamilton–Jacoby theory and the Bohr–Sommerfeld quantization rule[5] to the rotating Tietz–Hua oscillator and obtained expressions for rotational–vibrational levels that are much more realistic [when tested against the RKR (Rydberg–Klein–Rees) and ab initio calculations] at moderate and high quantum numbers than the corresponding levels obtained from Eq. (2). The main goal of this work is to derive, applying the approach of Paper I to the rotating Morse oscillator, energy expressions that are easy to use and highly accurate in the entire range of the vibrational and rotational quantum numbers of the O_2, N_2, NO, and CO molecules in their ground electronic states. We focus in this work on these four molecules because of their importance in environmental, plasma processing, and high-energy flow research, and because the approach of Paper I is very accurate in the case of these molecules. (The approach of this work can also be applied to diatomic molecules other than the O_2, N_2, NO, and CO molecules, but in some diatomics, the mathematical simplifications and physical approximations made in the approach may lead to less accurate energy levels than those obtained in this work.)

We discuss three expressions for rotational–vibrational levels of the four diatomic molecules under consideration. The first expression (representing our model A of molecular rotational–vibrational motion) is the truncated series expansion solution of the Schrödinger equation for the rotating Morse oscillator. The second expression is a relationship obtained from applying the approach of Paper I to the rotating Tietz–Hua oscillator (model B), and the third expression, the main result of this work, is obtained from applying the approach to the rotating Morse oscillator (model C).

II. Rotational–Vibrational Levels

A. Model A

In model A, the intramolecular potential of the rotating oscillator representing the diatomic molecule is

$$V^A_{ef}(R) = D[1 - e^{-\beta(R-R_e)}]^2 + \frac{L^2}{2\mu R^2} \tag{1}$$

where D is the well-depth of the potential, R_e is the molecular bond length, R is the internuclear distance, β is the Morse constant, μ is the reduced mass, and L is the angular momentum of the molecule. The first part of the sum in relationship (1) is the potential energy (the Morse potential) of the rotationless molecule, and the second part is the centrifugal energy of the rotating molecule (the rotating Morse oscillator).

The rotational–vibrational energies obtained from the solution of the Schrödinger equation for the diatomic molecule driven by potential (1) can be given as a series expansion, and the most common (truncated) form of the expansion is[4]

$$E^A_{v,J} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + B_e J(1 + J) - D_e J^2(1 + J)^2 \tag{2}$$

where ω_e, $\omega_e x_e$, B_e, and D_e are the usual spectroscopic constants, and J and v are the molecular rotational and vibrational quantum numbers, respectively. As mentioned earlier, Eq. (2) is inaccurate in diatomic molecules with moderate and high values of the rotational and vibrational quantum numbers.

Even though more accurate (higher-order) expansions of the solution of the Schrödinger equation for diatomic molecules

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Table 1 Molecular constants used in the present calculations[a]

Molecule	ω_e	$\omega_e x_e$	R_e	$\mu/10^{-23}$	D	b_h
$O_2(X^3\Sigma_g^-)$	1580.2	11.98	1.207	1.337	42,041	2.59103
$N_2(X^1\Sigma_g^+)$	2358.6	14.32	1.097	1.171	79,885	2.78580
$NO(X^2\Pi_r)$	1904.2	14.07	1.151	1.249	53,341	2.71559
$CO(X^1\Sigma^+)$	2169.8	13.29	1.128	1.146	90,531	2.20481

[a] ω_e, the vibrational constant, in cm^{-1}, $\omega_e x_e$, the anharmonicity constant, in cm^{-1}; R_e, the molecular bond length, in Å; μ, the reduced mass, in g; D, the well depth of the intramolecular potential, in cm^{-1}; note that in the text, D was used in cgs units. b_h is the parameter defined in Eq. (6).

have been discussed in literature, expression (2) is the most common in applications [this is the main reason (see Paper I) we compare this expression (instead of a higher-order expansion) with the results of the present work]. The popularity of expression (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 $\omega_e x_e$ 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).

The vibrational constants of the Morse oscillator are

$$\omega_e = \beta \left(\frac{D}{2\pi^2 c^2 \mu} \right)^{1/2} \tag{3}$$

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu} \tag{4}$$

where ω_e and $\omega_e x_e$ are in cm^{-1}, and the rest of the quantities are in units of the cgs system. However, it should be kept in mind that the constant β obtained from expression (3) will differ from that resulting from expression (4), if the spectroscopic constants ω_e, $\omega_e x_e$, and D are taken as the best available in literature, because the latter constants (typically, the constants are obtained from measurements and ab initio calculations) are not consistent with the model of the Morse oscillator. In the present work, we calculate β from relationship (3), because the constants ω_e and D are usually more accurate than the constants $\omega_e x_e$. The anharmonicity constants $\omega_e x_e$ used in the present calculations (Table 1) are the best available in literature.

B. Model B

Model B of the rotational–vibrational motion of diatomic molecules is based on a semiclassical formalism combining the Hamilton–Jacoby theory and the Bohr–Sommerfeld quantization rule (Paper I). The model (the rotating Tietz–Hua oscillator) assumes that the internuclear potential of a diatomic molecule is

$$V_{ef}^B(R) = D \left[\frac{1 - e^{-b_h(R-R_e)}}{1 - c_h e^{-b_h(R-R_e)}} \right]^2 + \frac{L^2}{2\mu R^2} \tag{5}$$

where c_h is an optimization parameter (Table 1) discussed in Paper I, and

$$b_h = \beta(1 - c_h) \tag{6}$$

The first part of sum (5) is the potential energy of the rotationless oscillator (the Tietz–Hua potential), and the second part is, as in the case of the rotating Morse oscillator, the molecular centrifugal energy.

The approach of Paper I leads to the following expression for the rotational–vibrational energies of diatomic molecules according to the model of the rotating Tietz–Hua oscillator:

$$E_{v,J}^B = D + L^2 B_J B_J'' - (F_0 x_1 - F_1'' - F_2''' L^2 - F_3''' L^4)^2 \tag{7}$$

where

$$B_J = \frac{\omega_2}{(b_h R_*)^4} \tag{8}$$

$$B_J'' = (b_h R_*)^2 - b_h R_*(7u^2 + 2u + 3) + 15u^2 + 6u + 3 \tag{9}$$

$$u = c_h \xi_{e*} \tag{10}$$

$$\xi_{e*} = \exp[-b_h(R_* - R_e)] \tag{11}$$

$$R_* = R_e + (B_h C_J + D_h C_J^2)/b_h \tag{12}$$

$$C_J = \frac{b_h^2 L^2}{2\mu D} \tag{13}$$

$$B_h = \frac{(1 - c_h)^2}{(b_h R_e)^3} \quad \text{and} \quad D_h = \frac{3}{2} B_h^2 - 3\frac{B_h^2}{b_h R_e} + 3\frac{B_h c_h(1 - c_h)}{(b_h R_e)^3} \tag{14}$$

$$F_0 = \hbar b_h/\sqrt{2\mu} \tag{15}$$

$$F_1'' = \sqrt{D}(1 + \omega_0 x_1 + \omega_1 x_1^2) \tag{16}$$

$$F_2''' = A_J(1 + \omega_0 x_2 + \omega_0^2 x_2^2) \times \left[-\eta_{1J} + \frac{\eta_{2J}}{\xi_{e*}}(1 + \omega_0 x_2 + \omega_1 x_2^2) \right] \tag{17}$$

$$F_3''' = \frac{A_J \eta_{2J}}{\xi_{e*}\sqrt{D}}(1 + \omega_0 x_2 + \omega_0^2 x_2^2) \times \left[F_2''' + \frac{A_J \eta_{2J}}{2\xi_{e*}}(1 + \omega_0 x_2 + \omega_1 x_2^2) \right] \tag{18}$$

$$x_1 = v + 1/2 \tag{19}$$

$$x_2 = (v_{\text{max}}^{\text{TH}} + 1)/2 \tag{20}$$

$$\omega_0 = \frac{\hbar b_h c_h}{\sqrt{2\mu D}} \tag{21}$$

$$\omega_1 = \omega_0^2 \left(1 - \frac{1}{2c_h} \right) \tag{22}$$

$$\omega_2 = b_h^2/2\mu \tag{23}$$

$$A_J = \omega_2/2\sqrt{D}\xi_{e*}(b_h R_*)^4 \tag{24}$$

$$\eta_{1J} = b_h R_*(20u^2 + 6u + 4) - (42u^2 + 18u + 6) \tag{25}$$

$$\eta_{2J} = b_h R_*(18u^2 + 14u + 1) - (36u^2 + 30u + 3) \tag{26}$$

$$L^2 = \hbar^2[J(J + 1) - \Lambda^2] \tag{27}$$

Λ is the quantum number for the axial component of the molecular electronic angular momentum, and the maximum value

$v_{\rm max}^{\rm TH}$ of the vibrational quantum number in the Tietz–Hua oscillator is the integer nearest to, and smaller than

$$v_{\rm max}^{\rm TH} = \frac{1 - c_h - (1 - 3c_h^2)^{1/2}}{\omega_0(2c_h - 1)} - \frac{1}{2} \tag{28}$$

C. Model C

The intramolecular potential of a diatomic molecule in model C is the same as that given in relationship (1). Applying the approach of Paper I to the model gives the following rotational–vibrational energies of the diatomic molecule:

$$E_{v,J}^{C'} = D + \hbar^2 A_M J(J + 1) - \left\{\frac{\beta\hbar(v + 1/2)}{(2\mu)^{1/2}} - \frac{2De^{(u_e - u_*)} - \hbar^2 B_M J(J + 1)}{2[De^{2(u_e - u_*)} - \hbar^2 C_M J(J + 1)]^{1/2}}\right\}^2 \tag{29}$$

where

$$u_e = \beta R_e \quad \text{and} \quad u_* = \beta R'_* \tag{30}$$

$$\xi'_{e*} = \exp[-\beta(R'_* - R_e)] \tag{31}$$

$$R'_* = R_e + (B'_h C_J + D'_h C'^2_J)/\beta \tag{32}$$

$$C'_J = \frac{\beta^2 L^2}{2\mu D}$$

$$B'_h = \frac{1}{(\beta R_e)^3} \quad \text{and} \quad D'_h = \frac{3}{2} B'^2_h - 3\frac{B'^2_h}{\beta R_e} \tag{33}$$

$$A_M = \frac{1}{2\mu(R'_*)^2}\left[1 - \frac{3}{\beta R'_*}\left(1 - \frac{1}{\beta R'_*}\right)\right] \tag{34}$$

$$B_M = \frac{2}{\mu\beta(R'_*)^3}\left(1 - \frac{3}{2\beta R'_*}\right) \tag{35}$$

$$C_M = \frac{1}{2\mu\beta(R'_*)^3}\left(1 - \frac{3}{\beta R'_*}\right) \tag{36}$$

Expression (29) can be further simplified by expanding the following function

$$f(L^2) = \frac{2D\xi'_{e*} - B_M L^2}{2\sqrt{D\xi'^2_{e*} - C_M L^2}} = \frac{2De^{u_e - u_*} - \hbar^2 B_M J(J + 1)}{2[De^{2(u_e - u_*)} - \hbar^2 C_M J(J + 1)]^{1/2}} \tag{37}$$

into power series about $L^2 = 0$, which leads to

$$f(L^2) \simeq \sqrt{D} + F_m L^2 + G_m L^4 + \cdots \tag{38}$$

where

$$F_m = \frac{1}{2\xi'_{e*}\sqrt{D}}\left(\frac{C_M}{\xi'_{e*}} - B_M\right) = \frac{\beta^2}{4\xi'^2_{e*}\mu u_*^3} \times \left[1 - 4\xi'_{e*} + \frac{3}{u_*}(2\xi'_{e*} - 1)\right] \tag{39}$$

$$G_m = \frac{C_M}{4\xi'^3_{e*} D\sqrt{D}}\left(-B_M + \frac{3C_M}{2\xi'_{e*}}\right) = \frac{\beta^4}{32\mu^2\xi'^4_{e*} D\sqrt{D} u_*^6}\left(1 - \frac{3}{u_*}\right) \times \left[3 - 8\xi'_{e*} + \frac{3}{u_*}(4\xi'_{e*} - 3)\right] \tag{40}$$

and, subsequently, to

$$E_{v,J}^{C''} = D + A_M L^2 - \left[\frac{\beta\hbar}{\sqrt{2\mu}}\left(v + \frac{1}{2}\right) - \sqrt{D} - F_m L^2 - G_m L^4\right]^2 \tag{41}$$

or

$$E_{v,J}^{C''} = f_b(v) + g_a(J) + g_b(J) + h(v, J) \tag{42}$$

where

$$f_b(v) = \frac{2\hbar\beta}{\sqrt{2\mu}}\sqrt{D}\left(v + \frac{1}{2}\right) - \frac{\hbar^2\beta^2}{2\mu}\left(v + \frac{1}{2}\right)^2 \tag{43}$$

$$g_a(J) = \frac{L^2\beta^2}{2\mu u_*^2}\left[1 - \frac{3}{u_*}\left(1 - \frac{1}{u_*}\right)\right] - 2\sqrt{D} f_a(J) \tag{44}$$

$$g_b(J) = \frac{-L^4\beta^4}{16\mu^2\xi'^4_{e*} D u_*^6}\left(1 - \frac{3}{u_*}\right)\left[3 - 8\xi'_{e*} + \frac{3}{u_*}(4\xi'_{e*} - 3)\right] - f_a^2(J) \tag{45}$$

$$h(v, J) = \frac{2\hbar\beta}{\sqrt{2\mu}}\left(v + \frac{1}{2}\right) f_a(J) \tag{46}$$

$$f_a(J) = \frac{L^2\beta^2}{4\xi'^2_{e*}\sqrt{D}\mu u_*^3}\left[1 - 4\xi'_{e*} + \frac{3}{u_*}(2\xi'_{e*} - 1)\right] \tag{47}$$

Expression (42) can be further simplified by noting that the dependence of the function $h(v, J)$ on the vibrational quantum number is not strong, especially at moderate and high values of v. Thus, assuming in expression (46) that $v = v_{\rm max}/2$, one has

$$E_{v,J}^{C'''} = f_b(v) + g_a(J) + g_b(J) + h_0(J) \tag{48}$$

where

$$h_0(J) = \frac{\hbar\beta}{\sqrt{2\mu}}(v_{\rm max} + 1) f_a(J) \tag{49}$$

and where the maximum value of the vibrational quantum number of the Morse oscillator is obtained from function (1), when $J = 0$. This value can be taken as the integer closest to, and smaller than

$$v_{\rm max} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \tag{50}$$

Expression (48) is very convenient in theoretical studies of molecular dynamics because it is quite accurate and it is given as a sum of molecular rotational energy (which depends only on the rotational quantum number J) and molecular vibrational energy (which depends only on the vibrational quantum number v). However, even though the replacement of v in Eq. (46) by $v_{\rm max}/2$ has little impact on the accuracy of expression (48) at moderate and high vibrational quantum numbers, it does cause some meaningful inaccuracy of the expression at low values of the quantum numbers.

III. Results and Discussion

As discussed in Paper I, the rotating Tietz–Hua oscillator is one of the most realistic analytical representations of rotational–vibrational dynamics of diatomic molecules. Therefore, we test the accuracy of the energy levels $E^A_{v,J}$, $E^B_{v,J}$, $E^C_{v,J}$, $E^{C'}_{v,J}$, and $E^{C''}_{v,J}$ of the O_2, N_2, NO, and CO molecules against the corresponding levels obtained from numerical solution of the Schrödinger equation for the rotating Tietz–Hua oscillator. [The testing can also be done against the levels obtained from the analytical solution (7) for the oscillator because the numerical and analytical solutions are very close (see Paper I).]

Figures 1–6 show the rotational–vibrational levels for all accessible quantum numbers of the O_2 and NO molecules. [The calculations of the levels were made for all four molecules (O_2, N_2, NO, and CO) discussed in this work, and the results for the N_2 and CO molecules (not shown in the figures) have accuracies that are very close to the accuracies of the results for the O_2 and NO molecules.]

As can be seen in Figs. 1 and 2, the accuracy of expression (29) obtained from the model C is very close, for all considered molecules and molecular levels, to the accuracy of expression (7), which was obtained from the model of the rotating Tietz–Hua oscillator. However, relationship (29) is more accurate than the truncated expression (2), obtained from the model of the rotating Morse oscillator.

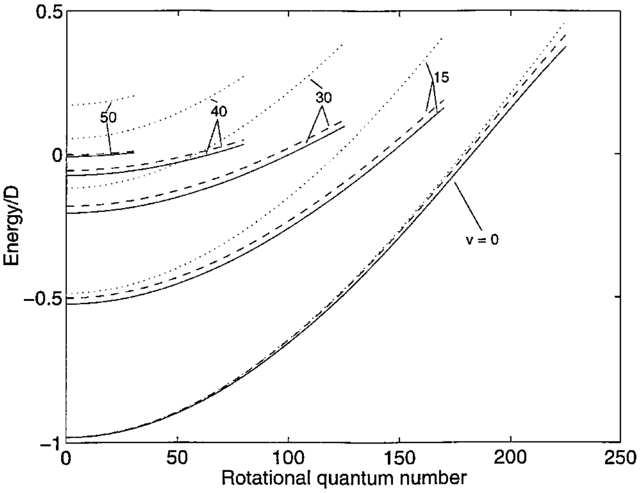

Fig. 1 Rotational–vibrational energies $E^B_{v,J}$ ——, Eq. (7); $E^A_{v,J}$ ·····, Eq. (2); and $E^C_{v,J}$ ---, Eq. (29), for the $O_2(X\,^3\Sigma_g^-)$ molecule. The zero rotational–vibrational energy corresponds to the dissociation continuum of the rotationless molecule. v and J are vibrational and rotational quantum numbers, respectively.

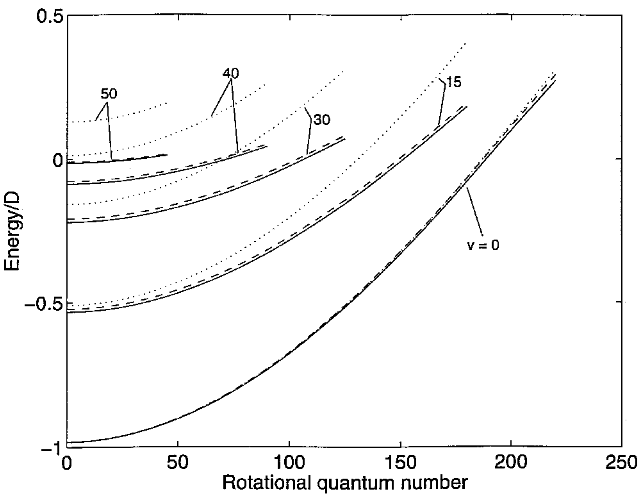

Fig. 2 Rotational–vibrational energies $E^B_{v,J}$ ——, Eq. (7); $E^A_{v,J}$ ·····, Eq. (2); and $E^C_{v,J}$ ---, Eq. (29), for the $NO(X\,^2\Pi_r)$ molecule. The meaning of the symbols is the same as in Fig. 1.

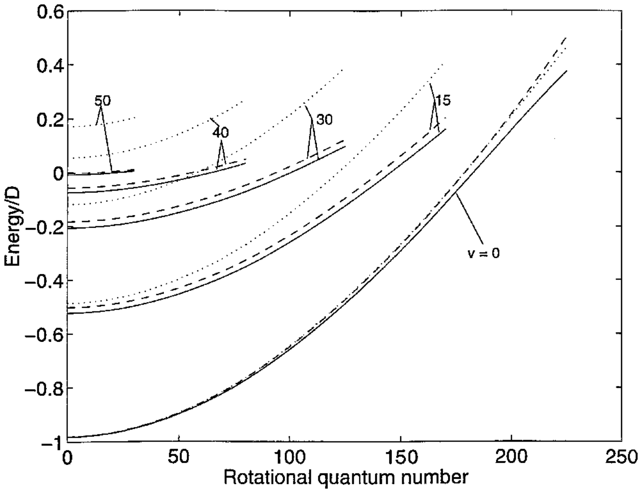

Fig. 3 Rotational–vibrational energies $E^B_{v,J}$ ——, Eq. (7); $E^A_{v,J}$ ·····, Eq. (2); and $E^{C'}_{v,J}$ ---, Eq. (41), for the $O_2(X\,^3\Sigma_g^-)$ molecule. The meaning of the symbols is the same as in Fig. 1.

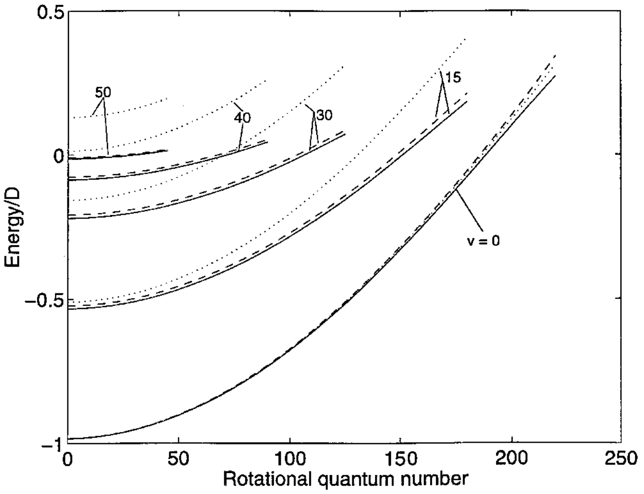

Fig. 4 Rotational–vibrational energies $E^B_{v,J}$ ——, Eq. (7); $E^A_{v,J}$ ·····, Eq. (2); and $E^{C'}_{v,J}$ ---, Eq. (41), for the $NO(X\,^2\Pi_r)$ molecule. The meaning of the symbols is the same as in Fig. 1.

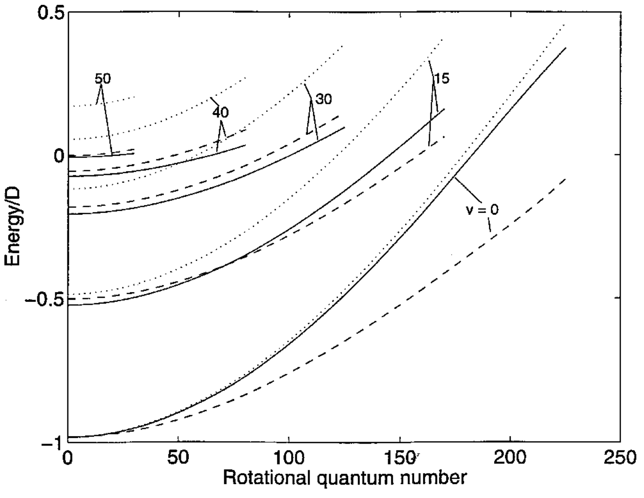

Fig. 5 Rotational–vibrational energies $E^B_{v,J}$ ——, Eq. (7); $E^A_{v,J}$ ·····, Eq. (2); and $E^{C''}_{v,J}$ ---, Eq. (48), for the $O_2(X\,^3\Sigma_g^-)$ molecule. The meaning of the symbols is the same as in Fig. 1.

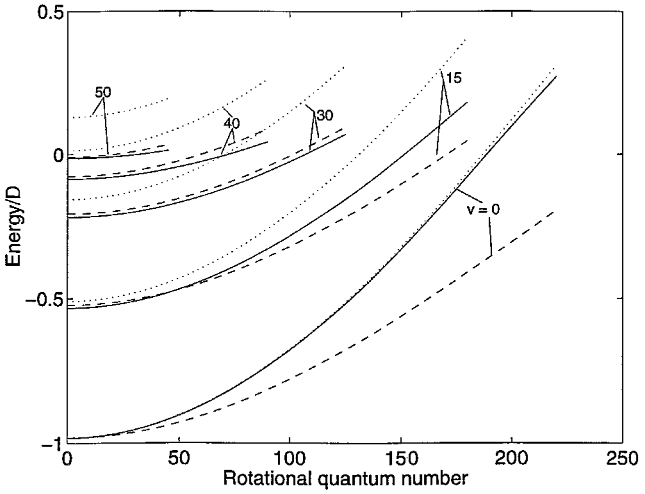

Fig. 6 Rotational-vibrational energies $E^B_{v,J}$, ——, Eq. (7); $E^A_{v,J}$, ·····, Eq. (2); and $E^{C'''}_{v,J}$ - - -, Eq. (48), for the NO(X^2P_r) molecule. The meaning of the symbols is the same as in Fig. 1.

Relationships (7) and (2) are compared with relationship (41) [a simplified version of Eq. (29)] in Figs. 3 and 4. The comparison shows that expressions (7) and (41) have similar accuracies and that these two expressions predict values of the moderate and high vibrational levels much more accurately than expression (2).

Comparison of Eqs. (7), (2), and (48) is shown in Figs. 5 and 6. One can see there that the substitution of $v_{\max}/2$ for v in Eq. (42) [the substitution leads to Eq. (48)] works quite well for vibrational levels higher than about $v_{\max}/3$.

In summary, expression (41) [or (42)] of this work is a reliable analytical approximation of molecular rotational-vibrational energies. Its accuracy is acceptable in most applications and in the entire range of molecular vibrational and rotational quantum numbers. In the case of molecules excited to states with quantum numbers greater than about $v_{\max}/3$, the expression can be replaced by relationship (48). From a practical point of view, the fact that formula (48) works well only at moderate and high vibrational quantum numbers is not a significant limitation, because one can use the formula at the moderate and high quantum numbers and simple expression (2), which is a sum of a v-independent term and a J-independent term, at low quantum numbers.

Acknowledgments

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