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A nonlinear Hamiltonian describing the rovibrational states of diatomic molecules

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Summary. On the basis of the deformable body model and harmonic potential approximation a nonlinear quantum-mechanical Hamiltonian describing rovibrational states of diatomic molecules has been derived. The obtained formula is applied in evaluation of molecular constants and for prediction of rovibrational and rotational spectra of the selected two-atomic systems giving quite satisfactory reproduction of the data values using only two molecular and one semiempirical parameters. This additional parameter is responsible for the change of curvature of internuclear potential in the excited rotational states, and may be viewed as an indicator of molecular susceptibility to rotation induced dissociation of a molecule.

Key words: Nonlinear Hamiltonian – Rovibrational transitions – Two-atomic molecule

1 Introduction

A two-atomic molecule is a simple example of the many body problem and it is the reason why it has been subject to extensive theoretical as well as experimental studies. The Born–Oppenheimer approximation divided the major problem into two parts, namely, the electronic part where electronic energy is calculated, and the rovibrational one where internal motion of the nuclei of a molecule is investigated.

The first part of the problem has been examined by *ab initio* calculations (see for example [1–5] and references cited therein), which explain the UV and visible spectra of diatomic molecules as well as some other physical properties such as polarizabilities [6], magnetizability [7] and so forth.

The second part, namely, the rovibrational states has been studied mostly by semiempirical methods (see for example [8–10]), and a few approaches have been proposed for assignment of the experimentally detected bands. The most popular are:

– The Dunham expansion method [11–13] where the rovibrational energy is expanded in a series of vibrational and rotational quantum numbers. This method, however, has two main disadvantages, namely, the power series has a poor convergency (sometimes it is necessary to use up to a dozen parameters, and, what is the most important, it cannot provide any information about the wavefunctions of individual states of a molecule, so matrix elements of various quantum-mechanical operators, the Franck–Condon factors and transitions intensities, cannot be directly calculated.

– The potential approach which introduces a semiempirical potential [14–18] to the rovibrational Hamiltonian, and the unknown parameters are to be obtained by a fit to experimental energy levels [16–25]. In contrast to the Dunham proposal, the above method provides the wavefunctions which are the solutions of the Schrödinger equation with a suitable internuclear potential.

The main question which arises from the above discussion is whether there exists a physically well-established model which is able to predict rovibrational transitions or justifies the expansion applied for assignment of the band observed, providing also the wavefunction of individual states of a molecule. A certain answer to the question brought up above has been obtained from the *soft body* model [26, 27], and the *deformable body* model [28] which lead to the same form of the rovibrational energy as that proposed by Watson [25], and ensure simultaneously a clear physical interpretation of all the terms obtained. The molecular models mentioned above are based on the assumption that positions of atoms in a molecule depend on the momentum and angular momentum as an effect of the deformational influence of the Coriolis and centrifugal forces acting in the rovibrational systems. Taking into account the above assumption and harmonic potential approximation, the nonlinear (in the quantum-mechanical sense) Hamiltonian was derived [28], which has not as yet been used in the rovibrational spectroscopy.

In view of the above, the main purpose of this paper is to employ the deformable body model and the nonlinear quantum-mechanical Hamiltonian in description of rovibrational and rotational spectra of the selected diatomic molecules. In particular it will be shown that two molecular and one semiempirical parameters are sufficient to obtain satisfactory reproduction of molecular spectra in a wide range of rotational states. The additional parameter may be applied as an indicator of molecular susceptibility to rotation induced dissociation of a molecule.

2 Nonlinear Hamiltonian of a two-atom system

The application of the deformable body model in description of rovibrational systems leads to the nonlinear [28] (in the quantum-mechanical sense) Hamiltonian:

$$\hat{H} = \tfrac{1}{2}\hat{\boldsymbol{P}}^T \boldsymbol{K}_0^{-1} \hat{\boldsymbol{P}} - \tfrac{1}{8}\hbar^2 Tr\boldsymbol{\mu}_0 + \tfrac{1}{2}\boldsymbol{\eta}^T(\hat{\boldsymbol{B}} + \boldsymbol{\Lambda})\boldsymbol{\eta} - \tfrac{1}{8}\hat{\boldsymbol{A}}^T(\hat{\boldsymbol{B}} + \boldsymbol{\Lambda})^{-1}\hat{\boldsymbol{A}}, \tag{1a}$$

$$\hat{\boldsymbol{A}} = \{\hat{\boldsymbol{P}}^T \boldsymbol{K}_k^{-1} \hat{\boldsymbol{P}} - \tfrac{1}{8}\hbar^2 Tr\boldsymbol{\mu}_k\}, \tag{1b}$$

$$\hat{\boldsymbol{B}} = \{\hat{\boldsymbol{P}}^T \boldsymbol{K}_{ks}^{-1} \hat{\boldsymbol{P}} - \tfrac{1}{8}\hbar^2 Tr\boldsymbol{\mu}_{ks}\}, \tag{1c}$$

$$Tr\boldsymbol{\mu} = \sum_\alpha \mu_{\alpha\alpha}, \quad \alpha = x, y, z, \tag{1d}$$

where $\hat{\boldsymbol{P}} = \{\hat{\boldsymbol{J}}, \hat{\boldsymbol{p}}\}$ and $\hat{\boldsymbol{J}}, \hat{\boldsymbol{p}}$ are the operators of the angular and vibrational momenta, $\boldsymbol{\Lambda}$ and $\boldsymbol{\eta} = \{\eta_k\}$ are the matrices of force constants and effective normal coordinates, whereas the kinematic matrices $\boldsymbol{K}_0^{-1}$, $\boldsymbol{K}_k^{-1}$ and $\boldsymbol{K}_{ks}^{-1}$ are defined in [28].

Let us consider a two-atom system endowed with a reduced mass m, in which vibrational displacements are described by the coordinate q canonically coupled with the vibrational momentum p. Employing the Taylor expansion of the reciprocal inertia tensor about the equilibrium distance q_0:

$$[m(q_0+q)^2] = (mq_0^2)^{-1} - 2(mq_0^3)^{-1}q + 3(mq_0^4)^{-1}q^2 - \cdots, \tag{2}$$

Hamiltonian (1a) for a two-atom system reduces to the simple form:

$$\hat{H} = \tfrac{1}{2}m^{-1}\hat{p} + \tfrac{1}{2}(\hat{\boldsymbol{B}}+\lambda)\eta^2 + \tfrac{1}{2}(mq_0^2)^{-1}\hat{\boldsymbol{J}}^2 - \tfrac{1}{8}\frac{\hat{\boldsymbol{A}}^2}{(\hat{\boldsymbol{B}}+\lambda)}, \tag{3a}$$

$$\hat{\boldsymbol{A}} = -2(mq_0^3)^{-1}\hat{\boldsymbol{J}}^2, \qquad \hat{\boldsymbol{B}} = 3(mq_0^4)^{-1}\hat{\boldsymbol{J}}^2, \tag{3b,c}$$

and substitution of the explicit form of operators $\hat{p} = -i\hbar\,\partial/\partial\eta$ [28], $\hat{\boldsymbol{A}}$ and $\hat{\boldsymbol{B}}$ yields:

$$\begin{aligned}\hat{H} = {} & -\hbar^2\frac{1}{2m}\frac{\partial^2}{\partial\eta^2} + \tfrac{1}{2}\lambda[3(mq_0^4\lambda)^{-1}\hat{\boldsymbol{J}} + 1]\eta^2 + \tfrac{1}{2}(mq_0^2)^{-1}\hat{\boldsymbol{J}}^2 \\ & - \tfrac{1}{2}(m^2q_0^6\lambda)^{-1}\hat{\boldsymbol{J}}^4[3(mq_0^4\lambda)^{-1}\hat{\boldsymbol{J}}^2 + 1]^{-1}.\end{aligned} \tag{4}$$

In order to solve the Schrödinger equation with nonlinear operator (3a) we propose the procedure which involves the following steps:

(i) Calculation of the "matrix" element $\langle v, J|\hat{\boldsymbol{B}}+\lambda|v, J\rangle$ in the base of harmonic oscillator and rigid rotor wavefunctions of the two-atom system.

(ii) Replacement of the nonlinear term $(\hat{\boldsymbol{B}}+\lambda)^{-1}$ in the Hamiltonian by the "matrix" element calculated in (i).

(iii) Averaging of the linear Hamiltonian over rotational states, in the base of rotational wavefunctions of diatomic molecules.

(iv) Solution of the vibrational Schrödinger equation by using the standard methods of quantum mechanics.

Having performed the above operations we arrive at the Schrödinger equation for harmonic oscillator, which can be directly solved:

$$\begin{aligned}\Big\{ & -\hbar^2\frac{1}{2m}\frac{\partial^2}{\partial\eta^2} + \tfrac{1}{2}\lambda[1 + CJ(J+1)]\eta^2 + BJ(J+1) \\ & \qquad - \frac{DJ^2(J+1)^2}{1+CJ(J+1)} - E_{vJ}\Big\}\psi_{vJ}(\eta) = 0,\end{aligned} \tag{5a}$$

$$E_{vJ} = \omega[1 + CJ(J+1)]^{1/2}(v + 1/2) + BJ(J+1) - \frac{DJ^2(J+1)^2}{1+CJ(J+1)}, \tag{5b}$$

$$\omega = \hbar(\lambda m^{-1})^{1/2}, \qquad B = \hbar^2(2mq_0^2)^{-1}, \tag{5c,d}$$

$$C = 3\hbar^2(m\lambda q_0^4)^{-1}, \qquad D = \hbar^4(2m^2q_0^6\lambda)^{-1}. \tag{5e,f}$$

$$\psi_{vJ} = N_{vJ}\exp[-1/2\gamma(J)\eta^2)]H_{vJ}[\gamma(J)^{1/2}\eta], \qquad \gamma(J) = m\hbar^{-1}\omega[1 + CJ(J+1)]^{1/2}, \tag{5g,h}$$

where $H_{vJ}[\gamma(J)^{1/2}\eta]$ is Hermite polynomial in $\gamma(J)^{1/2}\eta$.

The obtained results indicate that:

(i) The rovibrational energy of diatomic systems consists of an effective vibrational energy described by the first term in Eq. (5b), and an effective rotational energy given by the two last ones.

(ii) In the zero order approximation, considering a molecule as a rigid rotor ($\lambda = \infty$), the effective rotational energy reduces to the well-known formula $E_J = BJ(J+1)$.

(iii) For a small value of the constant C, the effective vibration and rotation energy can be expanded in a power series of $J(J+1)$, leading to the polynomial Dunham expansion [11] of the rovibrational energy of diatomic systems. In view of the above, the Dunham formula is a particular case of the general one given by the analytical expression of Eq. (5b).

(iv) The continued fraction formula of Eq. (5b) is a more general and stronger physically supported equation describing the rovibrational energy of two-atoms system, than the Dunham proposal.

The last point suggests the possibility of making some generalization of the formula obtained. Namely, instead of Eq. (5b) we propose to consider its simple extension given by the multiparametric continued fraction formula:

$$E_{vJ} = \omega_J[1 + C_J J(J+1)]^{1/2}(v + 1/2) + BJ(J+1) \quad - \cfrac{D_J J^2(J+1)^2}{1 + \cfrac{CJ(J+1)}{1 + \cfrac{xJ(J+1)}{1 + \cfrac{yJ(J+1)}{1 + \cdots}}}}, \tag{6a}$$

$$\omega_J = \omega \sqrt{1 + \cfrac{xJ(J+1)}{1 + \cfrac{yJ(J+1)}{1 + \cdots}}}, \qquad D_J = \cfrac{D}{1 + \cfrac{xJ(J+1)}{1 + \cfrac{yJ(J+1)}{1 + \cdots}}},$$

$$C_J = \cfrac{C}{1 + \cfrac{xJ(J+1)}{1 + \cfrac{yJ(J+1)}{1 + \cdots}}}, \tag{6b,c,d}$$

associated with the modified wavefunction:

$$\psi_{vJ} = N_{vJ} \exp[-1/2\gamma_J\eta^2] H_{vJ}(\gamma_J^{1/2}\eta), \qquad \gamma_J = m\hbar^{-1}\omega_J[1 + C_J J(J+1)]^{1/2}. \tag{7a,b}$$

Now, Eq. (6a) depends on two molecular parameters $\{q_0, \lambda\}$ i.e. equilibrium distance and force constant, respectively, as well as the set of additional semiempirical parameters $\{x, y, \ldots\}$, to be obtained by the fitting procedure.

The rovibrational transitions $v \to v+1$, $J \to J+1$ can be calculated from the equation:

$$\begin{aligned} \Delta E_{vJ} &= \omega_{J+1}[1 + C_{J+1}(J+1)(J+2)]^{1/2}(v + 3/2) \\ &\quad - \omega_J[1 + C_J J(J+1)]^{1/2}(v + 1/2) + 2B(J+1) \\ &\quad - \frac{D_{J+1}(J+1)^2(J+2)^2}{1 + C_{J+1}(J+1)(J+2)} + \frac{D_J J^2(J+1)^2}{1 + C_J J(J+1)}, \end{aligned} \tag{8}$$

whereas, the rotational energy in the vibrational state v and the energy of rotational transitions are described by the equations:

$$E_{vJ} = \omega_J[1 + C_J J(J+1)]^{1/2}(v + 1/2) + BJ(J+1) - \frac{D_J J^2(J+1)^2}{1 + C_J J(J+1)} - E_{v0}, \qquad (9a)$$

$$E_{v0} = \omega(v + 1/2), \qquad (9b)$$

$$\begin{aligned} \Delta E_{vJ} = {} & \omega_{J+1}[1 + C_{J+1}(J+1)(J+2)]^{1/2}(v + 1/2) \\ & - \omega_J[1 + C_J J(J+1)]^{1/2}(v + 1/2)2B(J+1) \\ & - \frac{D_{J+1}(J+1)^2(J+2)^2}{1 + C_{J+1}(J+1)(J+2)} + \frac{D_J J^2(J+1)^2}{1 + C_J J(J+1)}, \end{aligned} \qquad (9c)$$

where E_{v0} is the vibrational energy in the rotational state $J = 0$, and quantities ω_J, C_J, D_J are defined by Eq. (6b–d).

3 Applications

The obtained formulae will be applied to evaluate the molecular and semiempirical parameters $\{q_0, \lambda, x, y, z\}$, by fitting the experimental frequency values, which next will be used in calculation of rovibrational and rotational transitions of the selected diatomic molecules in the $^1\Sigma$ electronic state. The best values for the molecular parameters will be determined by the linear least-square routine in which the statistical weights, proportional to the inverse of experimental uncertainties, are taken as being equal to one. The calculated frequencies and the derived parameters are given with their sigma standard errors at the lower part of the tables and in parentheses, respectively. Moreover, the calculated frequencies are compared with those obtained applying the Dunham formula including comparable amount of fitted parameters. The results obtained are shown in Tables 1–3. Tables 1 and 2 present the observed minus calculated frequencies of rovibrational transitions (in cm^{-1}) for the $R(J)$ band of $^{12}C^{18}O$, $^{13}C^{16}O$, and $H^{81}Br$, $D^{79}Br$, whereas in Table 3 the results of calculations of rotational transitions (in MHz) for $H^{35}Cl$ and $H^{37}Cl$, molecules are collected. Tables 4 and 5 show the molecular and the Dunham parameters obtained by the fitting procedure and used in the assignment of molecular spectra as well as in derivation of the standard parameters, such as frequency of pure vibrational transitions ω, rotational constant B and centrifugal distortion constant D, defined by Eqs. (5c,d,f).

4 Conclusions

The application of the deformable body model and harmonic potential approximation has lead to the nonlinear Hamiltonian describing rovibrational states of a diatomic molecule. The proposed nonlinear Schrödinger equation can be strictly solved giving the exact analytic wavefunctions and eigenvalues reproducing quite well rovibrational and rotational transitions in wide range of rotational states. However, the accuracy of the calculations diminishes for molecules with high deformational susceptibility (HCl, HBr, DBr), i.e. for the systems which are characterized by a low value of the force constant and high amplitudes of vibrations. It is a consequence of using the harmonic potential and parabolic

Table 1. Energy of rovibrational transitions $\Delta E = E_{\text{exp}}{}^{a} - E_{\text{theor}}$ of CO molecule (in cm^{-1}) for $R(J)$ band, $v = 0 \rightarrow 1$

	$^{12}C^{18}O$			$^{13}C^{16}O$		
J	ΔE^{b}	ΔE^{c}	ΔE^{d}	ΔE^{b}	ΔE^{c}	ΔE^{d}
0	−3.1417	−0.0071	0.0229	−4.9876	−0.0153	0.0488
1	−2.5019	−0.0041	0.0137	−4.1836	−0.0101	0.0332
2	−1.9069	−0.0012	0.0065	−3.4275	−0.0044	0.0206
3	−1.3583	−0.0001	−0.0006	−2.7099	−0.0032	0.0061
4	−0.8543	0.0011	−0.0058	−2.0396	−0.0008	−0.0046
5	−0.3952	0.0022	−0.0093	−1.4118	0.0026	−0.0118
6	0.0180	0.0024	−0.0123	−0.8292	0.0046	−0.0183
7	0.3812	0.0035	−0.0128	−0.2908	0.0061	−0.0231
8	0.7116	0.0048	−0.0119			
9	0.9878	0.0031	−0.0130	−0.6524	0.0076	−0.0284
10	1.2205	0.0031	−0.0114	1.0577	0.0081	−0.0288
11	1.4084	0.0036	−0.0086	1.4177	0.0075	−0.0288
12	1.5488	0.0020	−0.0072	1.7379	0.0114	−0.0230
13	1.6465	0.0032	−0.0026	2.0058	0.0075	−0.0238
14	1.6955	0.0013	−0.0008	2.2329	0.0073	−0.0199
15	1.7000	0.0005	0.0023	2.4144	0.0060	−0.0162
16	1.6582	−0.0009	0.0047	2.5533	0.0070	−0.0095
17	1.5714	−0.0012	0.0079	2.6423	0.0029	−0.0076
18	1.4371	−0.0032	0.0092	2.6899	0.0023	−0.0017
19	1.2562	−0.0057	0.0094	2.6920	0.0012	0.0038
20	1.0332	−0.0041	0.0129	2.6471	−0.0017	0.0075
21	0.7630	−0.0034	0.0145	2.5580	−0.0037	0.0119
22	0.4434	−0.0056	0.0122	2.4244	−0.0042	0.0174
23	0.0797	−0.0054	0.0109	2.2450	−0.0051	0.0218
24				2.0191	−0.0070	0.0245
25	−0.7852	−0.0026	0.0063			
26	−1.2861	0.0007	0.0031	1.4302	−0.0100	0.0275
27	−1.8378	0.0002	−0.0059	1.0682	−0.0100	0.0286
28	−2.4319	0.0043	−0.0125	0.6582	−0.0118	0.0263
29	−3.0739	0.0082	−0.0221	0.2045	−0.0108	0.0250
30				−0.2953	−0.0093	0.0221
31				−0.8415	−0.0075	0.0174
32				−1.4339	−0.0051	0.0108
33				−2.0747	−0.0039	0.0004
35				−3.4904	0.0060	−0.0219
36				−4.2681	0.0123	−0.0366
37				−5.0885	0.0239	−0.0498
σ (cm^{-1})	1.6125	0.0039	0.0114	2.5430	0.0088	0.0244

[a] E_{exp} from Ref. [29]

[b] E_{theor} from Eq. (5b)

[c] E_{theor} from Eq. (6a) including one semiempirical parameter

[d] E_{theor} calculated from Dunham formula $E_{vJ} = \omega(v + 1/2) + J(J + 1)[B - \alpha(v + 1/2)]$

Table 2. Energy of rovibrational transitions $\Delta E = E_{\text{exp}}{}^{\text{a}} - E_{\text{theor}}$ of HBr molecule (in cm^{-1}) for $R(J)$ band, $v = 0 \rightarrow 1$

	$H^{81}Br$			$D^{79}Br$		
J	ΔE^{b}	ΔE^{c}	ΔE^{d}	ΔE^{b}	ΔE^{e}	ΔE^{f}
0	−34.4011	0.0050	−0.0016	−4.8542	0.0009	0.0806
1	−26.7908	−0.0004	−0.0023	−3.1064	−0.0205	0.0009
2	−19.7276	0.0001	0.0027	−1.6596	−0.0263	−0.0446
3	−13.2282	−0.0032	0.0012	−0.2427	−0.0141	−0.0558
4	−7.2916	−0.0024	0.0023	0.8850	0.0286	−0.0226
5	−1.9304	−0.0037	0.0001	1.7445	0.0343	−0.0152
6	2.8526	−0.0034	−0.0012	2.3665	0.0355	−0.0034
7	7.0525	0.0001	0.0004	2.7420	0.0249	0.0027
8	10.6584	0.0021	0.0005	2.8818	0.0153	0.0130
9	13.6595	−0.0019	−0.0051	2.7568	−0.0206	−0.0023
10	16.0638	0.0021	−0.0021	2.4479	0.0002	0.0367
11	17.8547	0.0038	−0.0007	1.8159	−0.0593	−0.0100
12	19.0278	0.0048	0.0008	1.0417	−0.0158	0.0376
13	19.5759	0.0042	0.0014	−0.0538	−0.0462	−0.0005
14	19.4929	0.0020	0.0010	−1.3098	0.0130	0.0357
15	18.7755	0.0007	0.0019	−2.8554	0.0354	0.0162
16	17.4135	−0.0035	−0.0002	−4.6998	0.0147	−0.0690
17	15.4140	0.0024	0.0074			
19	9.4193	−0.0153	−0.0094			
20	5.4472	−0.0047	−0.0001			
22	−4.5252	−0.0028	0.0014			
23	−10.5248	0.0092	0.0044			
24	−17.2182	0.0035	−0.0029			
25	−24.5934	0.0001	−0.0036			
26	−32.6545	−0.0045	0.0029			
σ (cm^{-1})	18.2887	0.0052	0.0036	2.7193	0.0309	0.0394

[a] E_{exp} for $H^{81}Br$ from Ref. [30], and for $D^{79}Br$ from Ref. [32]

[b] E_{theor} from Eq. (5b)

[c] E_{theor} from Eq. (6a) including three semiempirical parameters x, y, z

[d] E_{theor} calculated from Dunham formula $E_{vJ} = \omega(v + 1/2) + J(J + 1)[B - \alpha(v + 1/2)] - J^2(J + 1)^2 [D - \beta(v + 1/2)]$

[e] E_{theor} from Eq. (6a) including one semiempirical parameter x

[f] E_{theor} calculated from Dunham formula $E_{vJ} = \omega(v + 1/2) + J(J + 1)[B - \alpha(v + 1/2)]$

expansion of the reciprocal inertia tensor in derivation of the rovibrational Hamiltonian, which limit the application of the obtained formula to the low-excited vibrational states ($v = 0, 1$) of molecules.

For CO, DBr and HCl molecules satisfactory reproduction of the experimental data is obtained using only two molecular and one semiempirical parameters $\{q_0, \lambda, x\}$, whereas the same for HBr molecule requires the set of five parameters $\{q_0, \lambda, x, y, z\}$. It may be noted that application of the 2nd (6th for HBr) and following semiempirical parameters lowers the accuracy of calculations (CO), or does not change it remarkably (DBr, HBr, HCl), so, only Eq. (6a) which takes into account one (three for HBr) additional parameter seems to be a physically well supported equation.

Table 3. Energy of rotational transitions $\Delta E = E_{\mathrm{exp}}{}^{a} - E_{\mathrm{theor}}$ of HCl molecule (in MHz) for $R(J)$ band, v = 0

	$H^{35}Cl$			$H^{37}Cl$		
J	ΔE^{b}	ΔE^{c}	ΔE^{d}	ΔE^{b}	ΔE^{c}	ΔE^{d}
0	−30.906	0.029	0.040	−30.724	0.022	0.033
1	−53.768	−0.022	−0.005	−53.362	0.056	0.072
2	−61.663	0.090	0.104	−61.911	−0.535	−0.522
3	−51.149	−0.005	−0.003	−50.702	0.129	0.132
4	−22.434	−0.057	−0.068	−22.081	0.159	0.148
5	18.452	−0.013	−0.032	18.523	0.172	0.154
6	58.317	−0.066	−0.078	58.104	0.079	0.067
7	76.355	0.123	0.131	75.656	−0.110	−0.101
8	41.539	−0.040	−0.015	41.134	0.192	−0.167
9	−86.349	−0.002	−0.016	−85.699	−0.118	0.104
σ (MHz)	60.746	0.036	0.077	60.376	0.248	0.237

[a] E_{exp} from Ref. [31]
[b] E_{theor} from Eq. (5b)
[c] E_{theor} from (6a) including one semiempirical parameter x
[d] E_{theor} calculated from Dunham formula $E_{vJ} = \omega(v + 1/2) + J(J + 1)[B - DJ(J + 1)]$

Table 4. Ground state molecular parameters fitted to the experimental data

	σ	q_0 (Å)	$\lambda(\mathrm{N\,m^{-1}})$	$x^{a} \times 10^{5}$	ω	B	$D \times 10^{6}$
cm^{-1}	1.6125	1.22648(66)	1863.6(10)		2095.95	1.463561	5.8512
$^{12}C^{18}O$	0.0039	1.128795(54)	1856.7880(40)	−2.4643(11)	2092.13	1.837555	5.6703
29[b]					2117.399[c]	1.839113[c]	5.550[c]
cm^{-1}	2.5430	1.3004(80)	1867.0(14)		2101.90	1.389929	2.4311
$^{13}C^{16}O$	0.0088	1.129207(84)	1856.7117(80)	−2.4643(14)	2096.09	1.843244	5.7015
35					2121.439[c]	1.846151[c]	5.5931[c]
cm^{-1}	18.2887	2.062(49)	396.8(21)		2601.09	3.983281	37.366
$H^{81}Br$	0.0052	1.414143(85)	383.9249(15)	−31.325(14)[e]	2558.5186	8.46836	371.09
25		1.41443[d]			2648.975[d]	8.46488[d]	345.7[d]
cm^{-1}	2.7131	1.663(15)	394.65(57)		1846.74	3.103394	35.056
$D^{79}Br$	0.0309	1.41807(57)	391.726(11)	−15.213(45)	1839.89	4.268402	91.890
17							
MHz	60.746	1.290750(35)	475.08(84)		2869.01	10329173	535.54
$H^{35}Cl$	0.069	1.2852807(22)	494.4214(91)	−12.0683(48)	2926.82	10.417269	527.87
10		1.27455[d]			2990.946[d]	10.59341[d]	531.94[d]
MHz	1.213	1.584(12)	393.09(32)		1843.08	3.421858	47.179
$H^{37}Cl$	0.248	1.2852809(80)	494.408(32)	−12.031(17)	2924.57	10.315950	513.88
10							

[a] Parameters x, y, z are dimensionless
[b] Number of experimental data in fit
[c] Experimental data from Ref. [29]
[d] Experimental data from Ref. [10]
[e] Remaining semiempirical parameters for $H^{81}Br$ are $y = 6.014(53) \times 10^{-5}$, $z = -1.984(46) \times 10^{-4}$

Table 5. Dunham molecular parameters (cm^{-1}) fitted to the experimental data

	σ	B	D	$H \times 10^4$	ω	$\alpha \times 10^2$	$\beta \times 10^6$
$^{12}C^{18}O$	0.0114	1.84659(53)			2092.0871(67)	1.7293(31)	
$^{13}C^{16}O$	0.0244	1.85766(79)			2095.999(13)	1.7661(38)	
$H^{81}Br$	0.0036	8.4628(13)	$3.362(43) \times 10^{-4}$		2558.5331(44)	2.3147(30)	4.80(29)
$D^{79}Br$	0.0394	4.3253(46)			1839.735(32)	9.21530(45)	
$H^{35}Cl$[a]	0.077	312989.2386(88)	15.83037(16)	4.9240(87)			
$H^{37}Cl$[a]	0.237	312519.067(27)	15.78294(49)	4.924(27)			

[a] Parameters for $H^{35}Cl$ and $H^{37}Cl$ are calculated in MHz

The performed calculations indicate that for CO, DBr and $H^{35}Cl$ molecules multiparametric continued fraction formula of Eq. (6a) reproduces the energy of rovibrational and rotational transitions more precisely, than the Dunham expansion including a comparable number of the fitted parameters. However, in the case of the remaining molecules a slight difference in the accuracy of calculations is observed, which points to the advantage of the Dunham method.

A detailed analysis of Eqs. (6a–d) indicates that introduction of the additional parameter x is equivalent to the replacement $\lambda \rightarrow \lambda_J = \lambda[1 + xJ(J+1)]$ in the starting Eq. (5b). From the mathematical point of view the force constant describes the curvature of the internuclear potential function, whereas physically it may be interpreted as a measure of molecular rigidity. As the parameter x is negative for all the molecules considered, the molecular rigidity diminishes with the quantum number J, leading to the possibility of *rotation induced dissociation* in highly excited rotational states. Table 4 reveals that x diminishes with rigidity of a molecule, so the semiempirical parameter x may be considered as an *indicator* of molecular susceptibility to rotational dissociation.

Infrared and microwave spectra of diatomic molecules provide important information on their internal structure and physical properties. The well-resolved IR and MW spectra, as well as the structural simplicity of two-atomic systems are the reasons why they have become convenient test objects for theoretical calculation of molecular parameters and reproduction of molecular spectra. Usually a simple analysis of molecular rovibrational spectra has been realized in the framework of the potential or the Dunham approach. In the potential approach, energy levels are obtained by solving the Schrödinger equation with the interatomic potential expanded in terms of interatomic variables, and the potential coefficients are obtained either by a fit to the experimental energy levels or, if available, by a fit to a theoretically calculated potential. In the above method the solution of the Schrödinger equation provides the relevant wavefunctions. In the Dunham approach the rovibrational energy is expanded in terms of vibrational and rotational quantum numbers, and unknown semiempirical parameters are obtained by a fit to the experimental energy levels. The disadvantage of the Dunham approach is that a power series describing rovibrational energy has a poor convergence, and that Dunham expansion does not provide any information about the wavefunction of individual states of a molecule. The method developed in this work, which is based on the fraction continued Eq. (6a) including a set of *external* semiempirical parameters, appears to be the third method combining the potential and the Dunham approach, thus permitting to obtain analytical eigenvalues and eigenfunctions indispensable in a more sophisticated analysis of molecular spectra, and furthermore, allowing to calculate the matrix elements of quantum-mechanical operators, the Franck–Condon factors and transitions intensities, which is not directly possible within the standard Dunham approach.

The proposed method based on the deformable body model and harmonic potential can be easily extended [33–34] to include anharmonic potentials, for example Kratzer [16] or Simons–Parr–Finlan potential [17–19]. In this case the analytic eigenvalues and wavefunctions are obtained by solving the Schrödinger equation and next modified by the expanding dissociation constant into a continued fraction of rotational quantum number J.

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