

Ro-vibrational spectroscopy of molecules represented by a Tietz–Hua oscillator potential

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Abstract Accurate low and high-lying bound states of Tietz–Hua oscillator potential are presented. The radial Schrödinger equation is solved efficiently by means of the generalized pseudospectral method that enables optimal spatial discretization. Both $\ell = 0$ and rotational states are considered. Ro-vibrational levels of six diatomic molecules *viz.*, H₂, HF, N₂, NO, O₂, O₂⁺ are obtained with good accuracy. Most of the states are reported here for the first time. A detailed analysis of variation of eigenvalues with n , ℓ quantum numbers is made. Results are compared with literature data, wherever possible. These are also briefly contrasted with the Morse potential results.

Keywords Tietz–Hua oscillator · Ro-vibrational levels · Generalized pseudospectral method

1 Introduction

Construction of the universal potential energy function for molecules has been a challenging and active field of research in chemical physics. The reason for this is that the potential energy function succinctly carries the necessary informations relevant for a molecule. Thus, an enormous number of such functions have been proposed over the years, after the publication of three-parameter, exponential Morse potential [1] about 85 years ago. The literature is huge; the following reference gives some of the older as well as relatively newer empirical functions [1–18]. Usually, larger the number of parameters in the analytical potential energy function, better the fit with

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experimental data. While a few of these such as Morse, Mie-type and pseudoharmonic potentials offer *exact* analytic solutions [16, 17], most of these unfortunately can not be analytically solved for arbitrary vibrational and rotational quantum numbers. This necessitates the use of approximation schemes for their solutions.

Recently some attention has been paid on an analytic Tietz–Hua (TH) model potential [8, 11] for ro-vibrational levels in diatomic molecules, expressed in the following form,

$$v(r) = D \left[\frac{1 - e^{-b_h(r-r_e)}}{1 - c_h e^{-b_h(r-r_e)}} \right]^2; \quad b_h = \beta(1 - c_h), \quad (1)$$

where r_e relates to the molecular bond length, β the Morse constant, D signifies the potential well depth, r denotes the internuclear distance, while c_h implies an optimization parameter obtained from *ab initio* or Rydberg–Klein–Rees intramolecular potentials respectively. Note that in the limit of potential constant c_h approaching zero, TH potential reduces to the familiar Morse potential [1]. This potential supposedly describes the molecular dynamics (especially at high rotational and vibrational quantum numbers) more realistically than the traditional Morse potential [19–21]. Also it has been noted that this usually fits the experimental Rydberg–Klein–Rees curve more closely than the Morse function, especially near the dissociation limit [11, 19–21]. In another study, using Hamilton–Jacobi theory in conjunction with Bohr–Sommerfeld quantization rule, analytical expressions for rotational–vibrational levels of diatomic molecules within TH model have been derived [22]. Radial probability distributions of some diatomic molecules in excited rotational–vibrational states have also been reported using this route [23]. Very recently, *exact* analytical solution of the radial Schrödinger equation with TH potential has been provided for s waves within a parametric Nikiforov–Uvarov method [24]. In another development, approximate analytical solutions of the Dirac equation with TH potential were obtained for arbitrary spin-orbit quantum number using the Pekeris scheme [25].

The purpose of this work is to offer approximate solution of radial Schrödinger equation with TH potential for molecules. As already mentioned, the $\ell = 0$ states of this potential can be obtained in closed analytic form; while eigenvalues and eigenfunctions of $\ell \neq 0$ states of TH oscillator has not yet been reported in the literature, to the best of our knowledge. Here we take the help of generalized pseudospectral method (GPS) for an optimal effective discretization of the relevant Schrödinger equation. This method has produced very promising results for a number of situations having physical, chemical interest, including structure, dynamics in atomic and molecular physics. Accurate eigenvalues, eigenfunctions were obtained for low as well as higher states for a class of potentials such as spiked harmonic oscillators, logarithmic, rational, power-law, Hulthén, Yukawa, exponentially screened coulomb potentials, etc. [26–31]. Thus we make a detailed study on the bound-state spectrum of TH oscillator with particular reference to diatomic molecules. Ro-vibrational energies and radial densities are studied for both s -wave and *rotational* sates having *arbitrary* low and high vibrational quantum number. This will also enable us to judge the viability and feasibility of current approach in the context of diatomic molecular potentials. To this end, arbitrary $\{n, \ell\}$ states are reported for six molecules, *viz.*, H_2 , HF, N_2 , NO, O_2 , O_2^+ . Comparison with literature data are made wherever possible. The article is organized as follows.

A brief overview of the adopted method is given in Sect. 2. Then a discussion of the results is presented in Sect. 3, while we conclude with a few remarks in Sect. 4.

2 The GPS method

This method has been discussed in detail earlier (see the references [26–31] and therein). Thus it suffices to present here only a brief summary of the essential steps involved.

Without loss of generality, the desired time-independent radial Schrödinger equation, to be solved, can be written as (atomic units employed unless otherwise mentioned),

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{2r^2} + v(r) \right] \psi_{n,\ell}(r) = E_{n,\ell} \psi_{n,\ell}(r) \tag{2}$$

where $v(r)$ is the TH potential, as given in Eq. (1), while n, ℓ signify the radial and angular momentum quantum numbers respectively. The GPS formalism facilitates the use of a denser mesh at small distance and relatively coarser mesh at large distance preserving similar accuracy at both the regions.

A key step in this approach is to approximate a function $f(x)$ defined in the interval $x \in [-1, 1]$ by an N -th order polynomial $f_N(x)$ exactly at the discrete collocation points x_j ,

$$f(x) \cong f_N(x) = \sum_{j=0}^N f(x_j) g_j(x), \quad f_N(x_j) = f(x_j). \tag{3}$$

Within the Legendre pseudospectral method that we are using currently, $x_0 = -1, x_N = 1$, and x_j 's ($j = 1, \dots, N - 1$) are determined from the roots of first derivative of the Legendre polynomial $P_N(x)$ with respect to x , i.e., $P'_N(x_j) = 0$. The $g_j(x)$ s in Eq. (3) are termed the cardinal functions expressed as,

$$g_j(x) = -\frac{1}{N(N + 1)P_N(x_j)} \frac{(1 - x^2) P'_N(x)}{x - x_j}, \tag{4}$$

satisfying the relation $g_j(x_j) = \delta_{j'j}$. At this stage, a transformation $r = r(x)$ is used to map the semi-infinite domain $r \in [0, \infty]$ onto the finite domain $x \in [-1, 1]$, along with an algebraic nonlinear mapping, $r = r(x) = L \frac{1+x}{1-x+\alpha}$, with $L, \alpha = 2L/r_{max}$ being two mapping parameters. Finally introducing a symmetrization procedure gives a transformed Hamiltonian of the following form,

$$\hat{H}(x) = -\frac{1}{2} \frac{1}{r'(x)} \frac{d^2}{dx^2} \frac{1}{r'(x)} + v(r(x)) + v_m(x). \tag{5}$$

The advantage lies in the fact that this leads to a *symmetric* matrix eigenvalue problem which can be solved readily and efficiently to give accurate eigenvalues, eigenfunctions

by using standard routines. Note that $v_m(x) = 0$ for the above transformation and one finally obtains a set of discretized coupled equations.

Considerable checks have been made on the convergence of eigenvalues with respect to the mapping parameters for a decent number of molecular states. After a series of such test calculations, a choice has been made at the point where the results changed negligibly with such variations. In this way, a consistent and uniform set of parameters ($r_{max} = 500$, $\alpha = 1$ and $N = 300$) has been used.

3 Results and discussion

At first, we present the calculated ro-vibrational levels within the TH model potential. For this six representative molecules, *viz.*, H₂, HF, N₂, NO, O₂, O₂⁺ are selected; the respective spectroscopic parameters, adopted from [22], are given in Table 1. The conversion parameters used in this work are taken from NIST database [32]. These are as follows: Bohr radius = 0.52917721092 Å, Hartree energy = 27.21138505 eV, and electron rest mass = 5.48577990946 × 10⁻⁴ u. However, before we proceed, note that this potential reduces to Rosen-Morse, Morse and Manning–Rosen potential for negative, zero and positive values of c_h respectively [22]. Thus two sets of calculations are performed for H₂ and HF in the limit of $c_h = 0$. The {0, 0}, {5, 0}, {7, 0} state energies at such limit are estimated to be -4.481469 (-4.481466), -2.220206 (-2.220195), -1.535804 (-1.535780) eV, where the numbers in the parentheses refer to similar energies reported in [24], obtained by means of a Nikiforov–Uvarov method. The first and second integer in square bracket identify the vibrational (radial) and rotational (angular) quantum numbers respectively. The same three states for HF molecule read as follows -5.868677 (-5.868710), -3.625307 (-3.625604) and -2.878718 (-2.878878). In both cases, our GPS results are found to be in excellent agreement with those from [24] and one notices that when the potential constant c_h tends to zero, TH energy levels approach that of the familiar Morse oscillator levels. This has been verified for other states as well. Now we present the main results for *s*-wave and rotational states for these six molecules in Table 2. Thus, nine low-lying bound-state energies corresponding to {0, ℓ }, {3, ℓ }, {5, ℓ }, having $\ell = 0, 1, 2$ are reported. In comparison to other molecular potentials, there is a visible lack of literature results for TH oscillator potential. No direct results are available for any of the non-zero angular momentum states. Only the $\ell = 0$ states having vibrational quantum

Table 1 Spectroscopic parameters of the molecules, used in present calculation, taken from [22]

Molecule	c_h	$\mu/10^{-23}$ (g)	$b_h(\text{Å}^{-1})$	$r_c(\text{Å}^{-1})$	$\beta(\text{Å}^{-1})$	$D_e(\text{cm}^{-1})$
H ₂	0.170066	0.084	1.61890	0.741	1.9506	38318
HF	0.127772	0.160	1.94207	0.917	2.2266	49382
N ₂	-0.032325	1.171	2.78585	1.097	2.6986	79885
NO	-0.029477	1.249	2.71559	1.151	2.7534	53341
O ₂	0.027262	1.377	2.59103	1.207	2.6636	42041
O ₂ ⁺	-0.019445	1.377	2.86987	1.116	2.8151	54688

Table 2 Calculated eigenvalues of TH potential for some low-lying states of six diatomic molecules along with literature data

$n \ell$	$E_{n,\ell} - D_e$ (eV)		$E_{n,\ell} - D_e$ (eV)		$E_{n,\ell} - D_e$ (eV)	
	PR	Literature	PR	Literature	PR	Literature
H ₂			HF		N ₂	
0 0	-4.4815797825	-4.481571826	-5.8687195228	-5.868757846	-9.7588058322	-9.7588029855
3	-3.0595425362		-4.4737571516		-8.9066675119	
5	-2.2815913849	-2.281533873	-3.6601740988	-3.660498629	-8.3595761578	-8.359551147
0 1	-4.4669801579		-5.8636625262		-9.7583155848	
3	-3.0474413866		-4.4692935886		-8.9061913507	
5	-2.2710928924		-3.6560952745		-8.3591095263	
0 2	-4.4379154622		-5.8535547327		-9.7573351069	
3	-3.0233638406		-4.4603723647		-8.9052390449	
5	-2.2502130058		-3.6479433575		-8.3581762808	
NO			O ₂		O ₂ ⁺	
0 0	-6.4959334209		-5.1163223113	-5.116333496	-6.6645714733	-6.6645687718
3	-5.8133374461		-4.5590745476		-5.9898565742	
5	-5.3795826206		-4.2058686976	-4.205982010	-5.5597008912	-5.559676435
0 1	-6.4955164040		-5.1159784440		-6.6641689327	
3	-5.8129354009		-4.5587436240		-5.9894673742	
5	-5.3791906688		-4.2055464879		-5.5593207256	
0 2	-6.4946823862		-5.1152907228		-6.6633638662	
3	-5.8121313267		-4.5580817907		-5.9886889893	
5	-5.3784067819		-4.2049020823		-5.5585604098	

PR signifies present result

number $n = 0, 5, 7$ have been reported very recently in a parametrically generalized Nikiforov–Uvarov formalism [24]. These are available for all the five molecular species except NO. In all ten occasions, GPS energies are found to be in very good agreement with the literature values. The slight discrepancy may be due to the slight differences in conversion factors used in [24]. Next, in Table 3, nine high-lying rovibrational energies are reported for all the 6 molecular species. Angular quantum number as high as $\ell = 30$ is considered. To the best of our knowledge, none of these states have been reported before and it is hoped that these could be useful for future referencing.

Next we proceed for a detailed investigation on the energy variations for three selected molecules *viz.*, H₂, HF and NO respectively. The top three panels (a), (b), (c) in Fig. 1 depict the variations of $E_{n,\ell} - D_e$ (in eV) with respect to the angular quantum number ℓ for H₂, HF and NO. These are given for six values of vibrational quantum number, *viz.*, $n = 0, 3, 6, 9, 12, 15$ for H₂; seven values of n ($n = 20$ in addition to all the six n in H₂) for HF; and nine values of n ($n = 25, 30$ in addition to all the seven n in HF) for NO. Note that the ℓ axis goes to 30 for H₂, while for the other two this is extended to 40. This happens because of the fact that a limited

Table 3 Calculated eigenvalues of TH potential for some high-lying states of six diatomic molecules

n	ℓ	$E_{n,\ell} - D_e$ (eV)	n	ℓ	$E_{n,\ell} - D_e$ (eV)	n	ℓ	$E_{n,\ell} - D_e$ (eV)
H ₂			HF			N ₂		
0	15	-2.9921666314	0	15	-5.2763995044	0	10	-9.7318505513
6		-0.9895676615	10		-1.6462931164	3		-8.8804871129
9		-0.3970747424	15		-0.6211626101	5		-8.3339200142
0	20	-2.1321131585	0	20	-4.8508452082	0	15	-9.7000161732
6		-0.4836490402	10		-1.3893569074	3		-8.8495689016
9		-0.0621445548	15		-0.4466120874	5		-8.3036216647
0	25	-1.2522963255	0	30	-3.7271155639	0	20	-9.6559768987
4		-0.3093944960	10		-0.7370870990	3		-8.8067988793
5		-0.1506049691	15		-0.0365890609	5		-8.2617104279
NO			O ₂			O ₂ ⁺		
0	10	-6.4730053894	0	10	-5.0974162346	0	10	-6.6424390361
3		-5.7912330333	3		-4.5408805335	3		-5.9684580465
5		-5.3580334807	5		-4.1881540596	5		-5.5387993854
0	15	-6.4459293673	0	15	-5.0750900921	0	15	-6.6163016863
3		-5.7651308474	3		-4.5193963303	3		-5.9431885057
5		-5.3325878765	5		-4.1672367007	5		-5.5141175736
0	20	-6.4084765984	0	20	-5.0442081090	0	20	-6.5801457931
3		-5.7290273103	3		-4.4896808485	3		-5.9082350230
5		-5.2973940820	5		-4.1383066355	5		-5.4799784798

PR signifies Present Result

number of bound states is supported by the potential. Such bound states occur in larger number for NO and HF than in H₂. It may be worthwhile mentioning here that, the maximum vibrational quantum number v_{\max} and maximum rotational quantum number ℓ_{\max} for H₂, HF, N₂, NO, O₂, O₂⁺ are (22,39), (28,66), (66,260), (56,230), (52,220) and (56,235) respectively [22]. The above v_{\max} 's are to be contrasted with the corresponding values of 18, 23, 82, 67, 65 and 58 in Morse potential for the six molecules under investigation [22]. Much larger differences in v_{\max} in TH potential (96) and Morse potential (174) have been observed in I₂, where the actual value is 107 [33]. The plots for other three molecules are omitted, as their qualitative characteristic features remain similar to one of the three plots in (a), (b), (c). As one moves along the H₂-HF-NO series, the plot for a given n series tends to vary rather slowly (rate of increase slows down), with H₂ and NO showing maximum and minimum increase respectively, such that for NO the plots are quite flat. Also for a given molecule, as one goes to higher n values, the separation between two successive n plots tends to decrease. Similar qualitative feature has been recorded earlier in the energy versus ℓ plot for H₂ within a semiclassical approach [22]. Now we turn to the $E_{n,\ell} - D_e$ (in eV) versus n for fixed ℓ quantum number for the same three molecules in the bottom panels (d), (e) and (f) respectively. The n axis in H₂, HF, NO extends to 25, 30 and 40. For H₂, these are studied at seven ℓ , viz., 0,5,10,15,20,25,30, while for the other two molecules

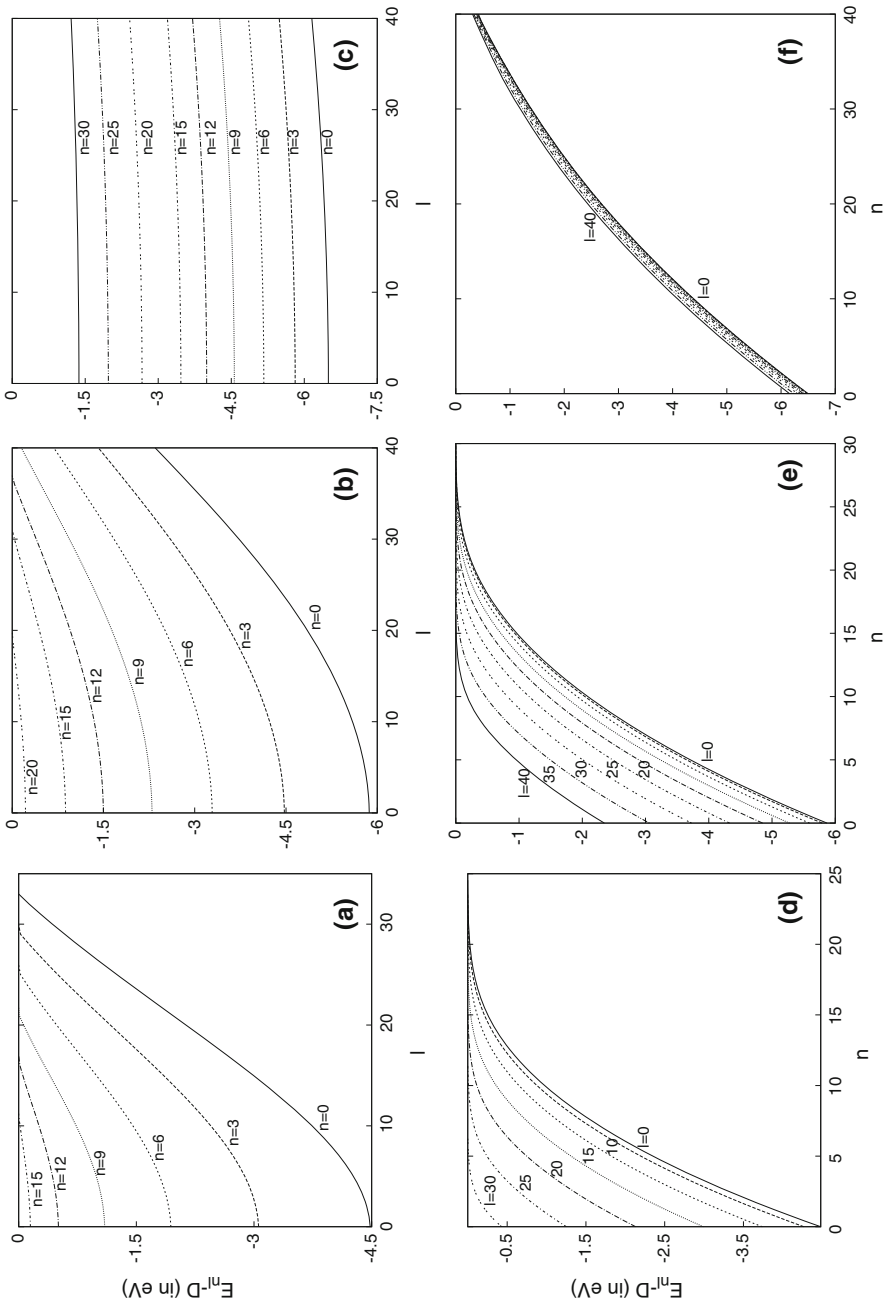


Fig. 1 Energy variations (in eV) in TH potential, with respect to rotational (l) (*top panel*) and vibrational (n) (*bottom panel*) quantum numbers respectively. The plots **a**, **d** correspond to H₂, while **b**, **e** and **c**, **f** correspond to HF and NO molecule respectively. State indices are indicated in the figure. See text for details

two more ℓ values of 35, 40 are considered besides the seven value of H_2 . In going from H_2 –HF–NO, the plots for different ℓ become progressively more closely spaced, with H_2 showing maximum sparsity and in NO the successive separations are too small to be identified properly in the scale. Another interesting feature is that, rate of increase in energy slowly increases as one moves the series, producing a nearly linear structure in NO. Also for H_2 , HF, as ℓ takes higher values, the separation between to adjacent ℓ tends to grow large. In both the ℓ and n plots in top and bottom panels, individual n and ℓ series for a given molecule remain nearly parallel to each other.

4 Conclusion

Tietz–Hua oscillator has been found to be a more realistic analytical potential than the familiar Morse potential in describing molecular dynamics at moderate as well as high rotational and vibrational quantum number. In the present work, we have presented both s –wave and rotational bound states having arbitrary rotational and vibrational quantum numbers with excellent accuracy. A total of 18 low and moderately high-lying ro-vibrational levels are given for six diatomic molecules, namely, H_2 , HF, N_2 , NO, O_2 , O_2^+ . While the lower states match quite well the lone literature result, many new states are given here for the first time. Energy changes with respect to n , ℓ quantum numbers are discussed in detail for three molecules. In short, a simple accurate and efficient scheme is offered for this and other similar potentials in molecular physics.

References

1. P.M. Morse, Phys. Rev. **34**, 57 (1929)
2. R. Rydberg, Z. Phys. **73**, 376 (1931)
3. N. Rosen, P.M. Morse, Phys. Rev. **42**, 210 (1932)
4. G. Pöschl, E. Teller, Z. Phys. **83**, 143 (1933)
5. M.F. Manning, N. Rosen, Phys. Rev. **44**, 953 (1933)
6. E.R. Lippincott, J. Chem. Phys. **21**, 2070 (1953)
7. A.A. Frost, B. Muslin, J. Chem. Phys. **22**, 1017 (1954)
8. T. Tietz, J. Chem. Phys. **38**, 3036 (1963)
9. J.N. Murrell, K.S. Sorbie, J. Chem. Soc. Faraday Trans. **70**, 1552 (1974)
10. D. Schiöberg, Mol. Phys. **59**, 1123 (1986)
11. W. Hua, Phys. Rev. A **42**, 2524 (1990)
12. A.N. Zavitsas, J. Am. Chem. Soc. **113**, 4755 (1991)
13. F.M. Rafi, Phys. Lett. A **205**, 383 (1995)
14. D.O.N. Gardner, L.v Szentpály, J. Phys. Chem. **103**, 9313 (1999)
15. P.G. Hajigeorgiou, R.J. Le Roy, J. Chem. Phys. **112**, 3949 (2000)
16. S.M. Ikhdair, R. Sever, J. Mol. Struct. (Theochem) **806**, 155 (2007)
17. S.M. Ikhdair, R. Sever, J. Mol. Struct. (Theochem) **855**, 13 (2008)
18. P.G. Hajigeorgiou, J. Mol. Spectrosc. **263**, 101 (2010)
19. R.T. Pack, J. Chem. Phys. **57**, 4612 (1972)
20. E. Levin, H. Partridge, J.R. Stallcop, J. Thermophys. Heat Transf. **4**, 469 (1990)
21. G.A. Natanson, Phys. Rev. A **44**, 3377 (1991)
22. J.A. Kunc, F.J. Gordillo-Vázquez, J. Phys. Chem. A **101**, 1595 (1997)
23. F.J. Gordillo-Vázquez, J.A. Kunc, J. Mol. Struct. (Theochem) **425**, 263 (1998)
24. M. Hamzavi, A.A. Rajabi, K.-E. Thylwe, Int. J. Quantum Chem. **112**, 2701 (2012)
25. S.M. Ikhdair, M. Hamzavi, Few-Body Syst. **53**, 473 (2012)
26. A.K. Roy, J. Phys. G **30**, 269 (2004)

27. A.K. Roy, *Int. J. Quantum Chem.* **104**, 861 (2005)
28. A.K. Roy, *Pramana-J. Phys.* **65**, 01 (2005)
29. A.K. Roy, A.F. Jalbout, E.I. Proynov, *J. Math. Chem.* **44**, 260 (2008)
30. A.K. Roy, *Int. J. Quantum Chem.* **113**, 1503 (2013)
31. A.K. Roy, *Results Phys.* **3**, 103 (2013)
32. The NIST reference on constants, units and uncertainty, physics.nist.gov/cuu/Constants/index.html
33. D.R.T. Appadoo, R.J. Le Roy, P.F. Bernath, S. Gerstenkorn, P. Luc, J. Verges, J. Sinzelle, J. Chevillard, Y.J. D'Aignaux, *J. Chem. Phys.* **104**, 903 (1996)