

Ionic Kratzer bond theory and vibrational levels for achiral covalent bond H₂

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Abstract. A 2-term dihydrogen Hamiltonian leads analytically to a quadratic Sommerfeld-Kratzer-potential and field quantization. Parameters ω_e , k_e and r_e for calculating H₂ vibrational levels derive solely from hydrogen mass m_H . Kratzer's ionic oscillator leads directly to the covalent H₂ bond energy and gives errors of 0,02 % for all H₂ levels, 30 times better than Dunham's oscillator, which gives 0,54 %. H₂ is prototypical for molecular spectroscopy, just like H is for atomic spectroscopy.

I. Introduction

Physicists focused on the *simple line spectrum* of atom H (with fine and hyperfine structure), less on the *complex band spectrum* of molecule H₂ [1]. Since Bohr's fairly accurate simple theory made atom H prototypical for atomic spectroscopy, one could expect that an equally simple theory would make bond H₂ prototypical for molecular spectroscopy [2]. Yet, only complex QM theory can account accurately for H₂-quanta, its vibrational levels and potential energy curve (PEC) [3,4]. This theory is not simple: it needs many parameters and 278 terms for the wave function of H₂ [3], which explains why simpler Bohr-type bond theories are still of interest [5].

QM cannot give a simple PEC-generating function or a *low parameter universal function* (UF), needed to unify observed shape-invariant, asymmetric PECs [2]. This failure justifies many attempts to find a UF, going on for decades [2,6]. The UF is probed with the smooth G(F)-plot of Varshni's F (for rotational constant α_e) and G (for vibrational constant $\omega_e x_e$) [6,7] in Dunham theory [8]. Since F and G quantify deviations from a *harmonic oscillator* (HO), the smooth G(F)-plot suggests that a UF, the *Holy Grail of Molecular Spectroscopy* [9], may exist [2,6]. Since a *universal bond* must be *prototypical for molecular spectroscopy*, the H₂ spectrum may lead to universal behavior, if any, provided its vibrational levels can be understood with a simple potential like Kratzer's [2,6].

Since anharmonicity and asymmetry in observed PECs flaw the HO, so important for modern physics [10], we discuss and review the HO respectively in Sections II and III. Section IV gives the ionic Kratzer bond theory for H₂, whereby all parameters needed (r_0 , ω_e and k_e) derive solely from mass m_H . Section V compares quantized Dunham and Kratzer oscillators as to precision for H₂ levels and covalent bond energy D_e . Discussion and conclusion are in Sections VI and VII.

II. Quantum HO and anharmonicity in bond H₂

H₂ rotator-vibrator levels $E_{v,j}$ depend on vibrational and rotational quantum numbers v and J . Since $E_{v,0}$ form the backbone of the H₂ PEC, we focus on $E_{v,0}$ (or $E_{v+1/2,0}$, if the zero point energy is used). For a quantum HO [11], equally spaced vibrational levels

$$E_{v+1/2} = \omega_e(v+1/2) \text{ cm}^{-1} \quad (1a)$$

with fundamental vibrational frequency ω_e , disagree with observed anharmonicity for H_2 (see Section I). A series expansion in half integer v

$$E_{v+1/2} = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 - \dots \text{cm}^{-1} \quad (1b)$$

gives agreement with observation but this is equivalent with an expansion in integer v

$$E_v = A+Bv+Cv^2+Dv^3 - \dots \text{cm}^{-1} \quad (1c)$$

Coefficients A, B, C... derive from those in (1b), e.g. $A=1/2\omega_e(1-x_e+y_e-\dots) \text{cm}^{-1}$ Fig. 1 gives the $E_v(v)$ plot for all 14 observed H_2 -levels in Table 1 [12]. Since 1st, 2nd, 4th and 6th order fits in v give errors of respectively 1839,93; 111,84¹; 7,15 and 0,24 cm^{-1} , even 6th order does not give *spectroscopic accuracy*. With errors of 1840 cm^{-1} , HO (1a) fails for the simplest, stable oscillator in nature, H_2 .

III. Revisiting the HO: Dunham and Kratzer potentials

Differential equation with sinusoidal solutions derive from Hooke force $F=-k_e r$, confronted with Newton's 2nd law $F=ma$ [11]. With $V(r)=1/2k_e r^2$, the Hooke-Dunham-type HO potential

$$V_{HO}=1/2k_e(r-r_0)^2=1/2k_e r_0^2(r/r_0-1)^2=a_0 d_D^2 \quad (2a)$$

is so firmly entrenched that alternatives are rarely employed, even when it is known to be wrong [2, 15]: *it is only accurate for r close to r_0 , it is symmetric instead of asymmetric and it can never converge*: it gives an infinity when $r \rightarrow \infty$. Its dimensionless Hooke-Dunham variable

$$d_D = (r/r_0-1) \quad (2b)$$

transforms (2a) in $V_{HO}=a_0 d_D^2$, where $V(r_0)=a_0=1/2k_e r_0^2$. Reduced $V'_{HO}=V_{HO}/a_0=d_D^2$ has 2 solutions $\pm d_D$ for the r -dependence in non-convergent, symmetric PECs. Although it adds flexibility to (2a) [7], even Dunham's series expansion in d_D with coefficients a_n [8]

$$V_{HO}=a_0 d_D^2(1+a_1 d_D+a_2 d_D^2+\dots) \quad (2c)$$

identical with $V(r)=c_1(r-r_0)+c_2(r-r_0)^2+c_3(r-r_0)^3+c_4(r-r_0)^4+\dots$, still faces convergence problems [7].

Despite this, (2c) is used in most studies to classify observed molecular constants $Y_{v,j}$ with a_n .

Variable (2b) calls for alternative dimensionless Sommerfeld-Kratzer variable [2]

$$d_{SK}=(1-r_0/r)=(1-1/d_D) \quad (2d)$$

which secures asymmetry as well as convergence *without expansions* [2,15]. Its oscillator potential

$$V_{SK}=1/2k_e r_0^2(1-r_0/r)^2=a_0(1-r_0/r)^2 \quad (2e)$$

in reduced form V_{SK}/a_0 gives 2 solutions for asymmetric, convergent PECs, i.e. $\pm d_{SK}$. For H lines and their fine structure, Sommerfeld introduced oscillator (2e) already in 1916 [16]. His pupil Kratzer used it for *a general bond theory* [17]; his colleague Kossel [18] for *an ionic bond theory*. Fues [19] solved the wave equation for (2e) [2,20] (the 4 were colleagues at Munich at the time).

¹ Morse-type 2nd order $E_v=-161,113+4397,264v-128,187v^2 \text{cm}^{-1}$ [13] gives large errors of 112 cm^{-1} (see [14]). A 4th fit $E_v=-8,076+4309,427v-135,295v^2+3,624v^3-0,202v^4$ still gives errors of 7 cm^{-1} (see Fig. 1 and further below).

The difference² between V_{HO} and V_{SK} shows with numerical variable x

$$x = r/r_0 = 1 + d_D = 1/(1 - d_{SK}) \quad (2f)$$

which has mathematical and physical percussions for oscillator theory (see below).

IV. First principles Bohr-type ionic Kratzer bond theory

IV.1 Hamiltonian for dihydrogen

The standard 10 term Hamiltonian \mathbf{H} for 4-particle system H_2 in QM (with pairs of charge-conjugated leptons a,b and nucleons A,B) has 4 kinetic³ and 6 potential energy terms

$$\mathbf{H} = \frac{1}{2}m_a v^2 + \frac{1}{2}m_b v^2 + \frac{1}{2}m_A v^2 + \frac{1}{2}m_B v^2 - \frac{e^2}{r_{aA}} - \frac{e^2}{r_{bB}} - \frac{e^2}{r_{bA}} - \frac{e^2}{r_{aB}} + \frac{e^2}{r_{ab}} + \frac{e^2}{r_{AB}} \quad (3a)$$

Yet, it cannot give simple analytical solutions for PECs and certainly not for the UF [22,23] (see Section I). The simplest Hamiltonian \mathbf{H} possible for diatomic H_2 is, by definition, diatomic

$$\mathbf{H} = \frac{1}{2}m_H v^2 + \frac{1}{2}m_H v^2 - A/r = +m_H v^2 - A/r \quad (3b)$$

It has only 2 terms: diatomic *kinetic energy* $+m_H v^2$ and *potential energy* $-A/r$, with distance r between 2 atoms, and constant A to be identified. *Two-particle Hamiltonian* for 2 *neutral atoms* (3b) is similar to Bohr's *two-particle Hamiltonian* for 2 *charged particles*. Field $-A/r$ seems suspicious for 2 *neutral atoms* but only at long range $r \gg r_0$. At close range, Coulomb interactions show but, in QM, these lead to the so-called *Coulomb problem* $+e^2/r_{ab}$, the electron-interaction term in (3a) [24].

An analytical solution for (3b) requires r - and ω -dependences. Atomic kinetic energy for periodic motion (vibrations on field axis r) relies on frequency ω and separation r to give *radial velocity*

$$v = \omega r \quad (3c)$$

where r is a *difference* between two points on the field axis. Using (3c) in (3b) leads to

$$\mathbf{H} = +m_H \omega^2 r^2 - A/r \quad (3d)$$

which allows a classical analytical analysis, formally similar to that of Bohr for atom H. A secondary axial axis, perpendicular to field axis r , is discussed elsewhere [21].

(i) The 1st derivative d/dr of (3d) gives forces $2m_H \omega^2 r$ and A/r^2 , securing

$$2m_H \omega^2 r^3 = 2m_H v^2 r = A \text{ and } v^2 = A/(2m_H r) \quad (3e)$$

At r_0 , $\omega = \omega_e$, $2m_H \omega_e^2 r_0^3 = 2m_H v^2 r_0 = A$ and $\mathbf{H}_0 = -m_H \omega_e^2 r_0^2 = -1/2 A/r_0 = -A/(2r_0)$ are the same formal classical virial results of Bohr for a rotating electron in atom H.

(ii) The 1st derivative $d/d\omega$ gives *radial momentum* $2m_H \omega r^2 = 2m_H v r$. Following Bohr, this is equal to an equi-dimensional constant of action like Planck's h (radial) or \hbar (angular), say fh , giving

$$2m_H \omega r^2 = 2m_H v r = fh \text{ and } v = fh/(2m_H r) \quad (3f)$$

with field scale factor f . Dividing (3e) by (3f) returns a velocity, equal to

²To not distract from H_2 , difference $d_D \pm 1/d_D$ between (2b) and (2d), referring to *chaos*, is discussed elsewhere [21]. Despite the indeterminacy for their ratio at r_0 , V_{HO} and V_{SK} are *anti-symmetric in their variables*. This indeterminacy cannot be used to veto a potential, as its basis is *mathematical*, not physical [21].

³Conventional v is used here to denote velocity, not to be confused with vibrational quantum v (see context).

$$v=A/(fh) \quad (3g)$$

similar to but numerically different from that in Bohr theory. Further similar results are

$$r=1/2f^2h^2/(m_H A) \text{ and } h\omega=A/(fr) \quad (3h)$$

For the *rotating electron* in Bohr H theory, $v=e^2/n\hbar=\alpha c/n$, where c is the velocity of light and α , the Sommerfeld fine structure constant, equal to $1/137,035999$ [16].

Constant $B=1/4f^2h^2/m_H$ transforms (3d) in

$$\mathbf{H}=-A/r+(1/4 f^2h^2/m_H)/r^2 = -A/r +B/r^2 \quad (3i)$$

With constant radial momentum, its 1st derivative gives $B=+1/2Ar_0$ and $\mathbf{H}=-A/r +1/2Ar_0/r^2$ or

$$\Delta\mathbf{H}=\mathbf{H}-\mathbf{H}_0=+(1/2A/r_0)(1-r_0/r)^2=V_{SK} \quad (3j)$$

i.e. the Sommerfeld-Kratzer potential (2d). Hence, V_{SK} stands for dihydrogen Hamiltonian \mathbf{H} (3b): no other terms are required and a wave equation is not yet needed [22]. Its repulsive term in $+(r_0/r)^2$ corresponds with kinetic energy in (3b). However, a classical solution for (3j) is only possible, if both A and r_0 were available classically too⁴ (see below).

(iii) The 2nd derivative d^2/dr^2 of (3d) for force constant equations $2m_H\omega_e^2$ and $2A/r_0^3$ gives

$$\omega_e^2=A/(m_H r_0^3) \quad (3k)$$

This implies that force constant k_e for *vibrations* in dihydrogen bond H_2 must be equal to

$$k_e=A/r_0^3 \quad (3l)$$

a first principles and analytical result, impossible with Hooke-Dunham oscillator theory.

[Although solutions above all have first principle's status, including (3k), reduced mass

$$\mu= m_H m_H / (m_H + m_H) = m_H / (1 + m_H / m_H) = 1/2 m_H \quad (3m)$$

should be used indeed of mass m_H . However, this is equivalent with using scale factor $s=1/2$ for dimer $H_2=H_A H_B$. More generally, dimensionless recoil correction

$$s=1/(1+m_A/m_B) \quad (3n)$$

for a diatomic with atoms (A, B) and masses (m_A, m_B) gives $s=1/2$ for dimers like H_2].

For simple \mathbf{H} (3b) to comply with HO theory and to identify A , force constant k_e in (2a) and (2e) must vary as $1/r^3$ for a $1/r$ law. If it were of Coulomb type [23], (3l) becomes

$$k_e=A/r_0^3=e^2/r_0^3 \quad (3o)$$

suggesting that *Coulomb attraction* $-e^2/r_0$, i.e. *ionic bond energy* D_{ion} , appears within *covalent* H_2 [2,23].

Plugging in observed $r_0=0,74 \text{ \AA}$ [25] in (3o) returns $k_e=5,7.10^5 \text{ dyne/cm}$ as observed and also reproduces observed $\omega_e \approx 4400 \text{ cm}^{-1}$ for H_2 [12,25], as shown recently [23]. While these quantitative results [23] obviously validate (3o) *a posteriori*, the problem of assessing r_0 classically must still be solved (see Section IV.2).

⁴ For rotations, angular momentum is readily quantized using Bohr's recipe but, since vibrations are the backbone of H_2 , e.g. its PEC, rotational states J are not considered here. Conform Bohr, H_2 *rotational frequency* ω varies with $\hbar/\mu r_0^2$.

Solution (3o) brings in *ionic bonding* at r_0 for *covalent bond* H_2 , since Kratzer's (3j) transforms in

$$\Delta H = H - H_0 = +(\frac{1}{2}e^2/r_0)(1 - r_0/r)^2 = V_{SK} \quad (3p)$$

This classical solution is soluble for any r but only provided r_0 is known. Analytical results (3j) and (3m) derive from dihydrogen Hamiltonian (3b), similar to Bohr's. Solution $A=e^2$ (3o) for velocity (3g) gives $v=(1/f)(e^2/h)$, which is discussed further in Section VI. Since PEC (3p) is *convergent and asymmetrical*, (3b) must be a convenient basis for a simple, classical bond theory, although *ionic Coulomb* potentials refer to old-fashioned *19th century ionic bonding theories* [2,18,22,23]. Analytically, (3j) proves that, whereas *not converging, symmetric Dunham oscillators* are typified with (2a) and variable $x=r/r_0$ (2f), *generic converging asymmetrical Coulomb Kratzer oscillators* obey (2d), (3h), (3p) and use inverse variable $1/x=r_0/r$. Coulomb oscillators like (3p) are perfectly symmetrical as well as harmonic in variable $1/x$ instead of x . This is the first principles classical Bohr-like *ionic Kratzer bond theory*, whereby the field must still be quantized (see below).

IV.2 Vibrational frequency, equilibrium separation of a Coulomb vibrator and quantum hypothesis for H_2

Calculating PEC (3p) is only possible when r_0 is known. For a Kratzer bond theory to remain classical, r_0 must be found classically too, which seems impossible. In any case, r_0 is needed to arrive at ω_e for H_2 from its force constant (3o) and its reduced mass, using

$$\omega_e = (1/2\pi)\sqrt{(k_e/\mu)} = (1/2\pi)\sqrt{[e^2/(\mu r_0^3)]} \quad (4a)$$

This major problem with r_0 for bond H_2 can nevertheless be solved with classical physics using the standard formula for spherical point-like particles with mass m_x , i.e.

$$m_x = (4\pi/3)\gamma_x r_x^3 \text{ g} \quad (4b)$$

with γ_x , the density (g/cm^3) and $4\pi/3$, the spherical form factor. Macroscopic model (4b) is reliable in classical physics but uncertainties emerge for microscopic systems: (a) *form factor and density*: is classical spherical model (4b) adequate for dihydrogen?; (b) *mass*: should total mass $2m_H$ or reduced mass $\frac{1}{2}m_H$ be used?; and (c) *size*: do results apply for r_0 in Coulomb's equilibrium energy $-e^2/r_0$ or for $2r_0$ in the virial's reduced energy $-\frac{1}{2}e^2/r_0$?

Electron and proton mass in NIST-tables [26] give $m_H = 1/(5,97538 \cdot 10^{23})$ g. With $\gamma_H = 1$, (4b) gives

$$r_H = [(3/4\pi)(m_H/\gamma_H)]^{1/3} \text{ cm} = 7,36516 \cdot 10^{-9} \text{ cm} = 0,736516 \text{ \AA} \quad (4c)$$

as classical radius r_H , whereas Bohr theory gives $r_B = 0,529177 \text{ \AA}$ (without recoil). Since $r_{HH} = 2r_H$, (4c) gives $r_0 = r_{HH} = 1,473032 \text{ \AA}$, typical for a virial rather than for a Coulomb energy (see above), knowing Huber and Herzberg give $r_0 = r_{HH} = 0,740144 \text{ \AA}$ [25]. Despite appearances, $\gamma_x = 1$ is a fair approximation for bound dihydrogen⁵ H_2 , viewed as a *dumb-bell* $\odot\odot$ with 2 spherical H atoms on field axis r at either side of the center of mass. The 2 sub-centers are positions of 2 nucleons

⁵ For systems with constant m_x/γ_x , r_x are (nearly) equal, as observed for isotopomers H_2 , D_2 and T_2 [25, 27].

at $-1/2r_0$ and $+1/2r_0$ from this center, i.e. a perfectly left-right anti-symmetric or *achiral* dumb-bell configuration (referred to in the title).

A *first principles ionic Kratzer bond theory* is now in reach to assess all H_2 vibrational levels. In fact, proceeding with (4a)-(4c), three important classical results immediately follow:

(i) with (4a) and (4c), the fundamental vibrational frequency⁶ for H_2 becomes

$$\omega_e = 4410,1722 \text{ cm}^{-1} \quad (4d)$$

where $4402,93 \text{ cm}^{-1}$ [12] or $4401,213 \text{ cm}^{-1}$ [25] are observed;

(ii) with (4c), the virial energy for H_2 is

$$-V_0 = e^2 / (2r_H) = a_0 = 78844,9125 \text{ cm}^{-1} \quad (4e)$$

(observed $a_0 = 1/2 k_e r_0^2 \approx 79000 \text{ cm}^{-1}$ [28]). By virtue of (4d)-(4e), an *unexpected 3^d result* is that

(iii) a natural *quantum hypothesis* for bond H_2 emerges. The small ratio of elementary *step* $\omega_e \sim 4400 \text{ cm}^{-1}$ (4d) and total gap $a_0 \sim 79000 \text{ cm}^{-1}$ (4e) suggests that a number of successive integer *steps*, say v as in (1c), is needed to cover this gap. The numerical ratio of step and gap

$$q = \omega_e / a_0 = 4410,1722 / 78844,9125 = 0,05593477 \quad (4f)$$

brings in quantization following *steps* δ_v , function of integer v , used to numerate the H_2 bands in the order they are observed [12]. The resulting *field quantum hypothesis for bonds* is

$$r / r_0 - 1 = \Delta / r_0 = d_{HO} = \delta_v = qv \quad (4g)$$

Dimensionless (4g) must be plugged into variables d_{HO} and d_{SK} for potentials V_{HO} and V_{SK} .

It is evident from (4f) and (4g) that product $a_0 \delta_v$ returns $a_0 qv = v \cdot 4410,1722 \text{ cm}^{-1}$, conform (1a).

With this ionic Kratzer bond theory, the only input needed to solve the complete Hamiltonian for covalent bond H_2 and its oscillator (3p) is absolute mass of hydrogen atom m_H . Since $m_H \approx 1/N \text{ g}$ (Avogadro $N = 6,023 \cdot 10^{23}$ [26]), r_0 for H_2 is even assessable from macroscopic experiments. In any case, m_H immediately provides with 3 fundamental quantities ω_e , r_0 and k_e for vibrator H_2 , an unprecedented result.

IV.3 Quantum hypothesis for vibrations in bond H_2

To apply (4g), field quantization is required. In Bohr theory, angular velocity v_e for a rotating electron with m_e (neglecting recoil) is obtained from a ratio of (i) radial equilibrium condition $m_e v_e^2 / r = e^2 / r^2$ and (ii) quantum hypothesis for *angular momentum* $m v_e r = n\hbar$, giving

$$v_e = m_e v_e^2 r / m_e v_e r = e^2 / (n\hbar) = \alpha c / n \quad (5a)$$

similar to (3e)-(3h) above. With Bohr radius r_B , quantized H-size r becomes

$$r = e^2 / m_e v_e^2 = n^2 \hbar^2 / (m_e e^2) = n^2 r_B \quad (5b)$$

Only, if Bohr had quantized the field (or the product of charges) as $-e^2 / n$ instead of angular momentum, the same energies $E_n = -R_H / n^2$ would have resulted, since

⁶ The same formula for an electron ($m_e = m_H / 1837,15267$ and radius r_B) gives $\omega_e = 219474,65 = 2 \cdot 109737,31 \text{ cm}^{-1}$, or twice the Rydberg e^2 / r_B [26]. This shows how the internal mechanics of H and H_2 are intimately connected.

$$v_e = m_e v_e^2 r / m_e v_e r = (e^2 / n) / \hbar$$

is *identical* with (5a). There is one important difference with Bohr H theory: *quantum rule*

$$e^2 / n \quad (5c)$$

brings in a *linear* n-dependence for H-size

$$r = \hbar / (m_e v_e) = n \hbar^2 / (m_e e^2) = n r_B \quad (5d)$$

instead of *quadratic* n^2 in (5b). Quantum rule (5c) therefore leads to a difference

$$r - r_B = (n-1) r_B = \ell r_B \quad (5e)$$

wherein Sommerfeld's secondary quantum number $\ell = n-1$ appears. Following (5e), quantization for H_2 proceeds according to a quantized difference⁷ Δ between 2 separations on the field axis

$$\Delta_r = r - r_0 = (n-1) r_0 \quad (5f)$$

linear, instead of quadratic, in an *integer quantum number*. Its reduced dimensionless equivalent

$$\Delta_r / r_0 = r / r_0 - 1 = (n-1) = \ell \quad (5g)$$

provides with a Bohr-like validation of the above *field quantum hypothesis for vibrations in bonds* (4g), be it in the context of a Hooke-Dunham r/r_0 theory. Since this differs from (1a) as well as from Kratzer's oscillator in r_0/r , validating (5g) depends on its implications for the H_2 band spectrum.

V. Quantization of symmetric linear and inverse field shifts in an achiral model

Multiplicative field scaling r_0/r or r/r_0 for Kratzer or Dunham models becomes additive, with inverse and linear relations

$$\begin{aligned} V_{SK}(r) / V_{SK}(r_0) &= r_0 / r = r_0 / (r_0 \pm \Delta) = 1 / (1 \pm \Delta / r_0) = 1 / (1 \pm \delta_r) \\ V_{HO}(r_0) / V_{HO}(r) &= r / r_0 = (r_0 \pm \Delta) / r_0 = (1 \pm \Delta / r_0) = (1 \pm \delta_r) \end{aligned} \quad (6a)$$

where δ_r or δ_v is the numerical equivalent of a step, quantized by (4g)-(5g). If Dunham's reduced field in (6a) were squared to give numerical parabola $(1 \pm \delta_r)^2$, first order effects would –unjustly– be doubled. Just like for its accompanying Hooke law, this entails factor $1/2$ for the asymptote, giving 1 for the linear Hooke term (force) but $1/2$ for the second order quadratic term (energy).

Rewriting total difference Δ between positions of 2 atoms on the field axis as

$$r - r_0 = +\Delta = +1/2 \Delta - (-1/2 \Delta) \text{ cm} \quad (6b)$$

shows that this difference is distributed in an anti-symmetric way, i.e. left and right to the center of mass, placed at the origin, but *equal in absolute magnitude* and based on the *arithmetic average*. In terms of symmetries, relation (6b) typifies *achiral, i.e. too symmetrical, bond theories* (see title).

However, (6b) in Dunham's model gives different results than Kratzer's, as expected from (6a).

⁷ Difference $\Delta = r - r_0$ brings in repetitions like $r = r_0 + \Delta = r_0 + (r - r_0) = r_0 + (r_0 + \Delta) - r_0 = r_0 + r_0 + (r - r_0) - r_0 = r_0 + r_0 + (r_0 + \Delta) - r_0 - r_0 \dots$, which are avoided with (5f). For N repetitions $r/r_0 = 1 + \Delta + N(+1-1)$, N *virtual pairs* (+1,-1) are created for a HO [29].

V.1 The v-dependence in achiral models: analytical form of quantized Dunham and Kratzer oscillators

(i) Symmetric distribution (6b), applied to Dunham's scaling procedure for $r=r_0\pm\Delta$, gives

$$r/r_0=1\pm\Delta/r_0=(1\pm\delta_r)=(1\pm\delta_v) \quad (6c)$$

on the basis of (5g). In this achiral case, the effect of a left-right difference is avoided by virtue of (6b). Symmetric Hooke-Dunham potential (2a) away from r_0 becomes

$$\frac{1}{2}k_\epsilon r_0^2(r/r_0)^2 = a_0(r/r_0)^2 = a_0(1\pm\delta_r)^2$$

With quantization rule (5g), reduced Dunham potential *differences* are

$$V_{HO}^v - V_0^v = \Delta V_{HO}^v = -\frac{1}{2}(1-qv)^2 + \frac{1}{2} = +qv - \frac{1}{2}q^2v^2 \quad (6d)$$

Using a_0 (4e) and q (4f), the numerical result of achiral Dunham H_2 theory in cm^{-1} is

$$\Delta V_{HO} = \Delta E_v = 4410,17v - 123,34v^2 \text{ cm}^{-1} \quad (6e)$$

close to 2nd order fit¹ in Section II but with relatively large errors of 100 cm^{-1} . The improvement over quantum HO (1a) is considerable but *spectroscopic accuracy* is far away. Morse's similar quadratic in $(v+1/2)$ is only moderately successful [7,14]. A parameter for qv cannot improve the goodness of this 2nd order fit. Apart from being more accurate than (1a), the advantage of (6e) over (1a) is still its simple first principles basis, where only m_H is used as input.

(ii) To apply field quantization for a Kratzer potential, there is a problem⁸ with anti-symmetric or left-right symmetric distribution (6b). Inverse $r_0/r = r_0/(1\pm\Delta)$ by virtue of (6a) and (6c) does not account for the positions of 2 atoms H_A and H_B with respect to the center, i.e. *achiral* distribution $\pm\frac{1}{2}\Delta$. Field quantization with Kratzer's r_0/r uses refined radial variables, given respectively by

$$r_A = r_0 - \frac{1}{2}\Delta \text{ and } r_B = r_0 + \frac{1}{2}\Delta$$

due to positional symmetry (achiral system). The Kratzer-Coulomb variable now becomes⁸

$$r_0(1/r_A - 1/r_B) = r_0(r_B - r_A)/r_A r_B = 1/(1 - \frac{1}{2}\delta_r) - 1/(1 + \frac{1}{2}\delta_r) = \delta_r / (1 - \frac{1}{4}\delta_r^2) \quad (6f)$$

Using bond quantum hypothesis (5g), the quantized v-dependence for Kratzer variable (6f) is

$$1/(1 - \frac{1}{2}qv) - 1/(1 + \frac{1}{2}qv) = qv / (1 - \frac{1}{4}q^2v^2) \quad (6g)$$

⁸ Despite appearances, an additional classical constraint for differences between 2 so-called equal bonding partners H_a and H_b in dihydrogen H_aH_b is available, if they are distinguished formally by mass m_a and m_b as well as by their positions on the field axis r_a and r_b . As in a balance, reduced mass is based on classical

$$m_a r_a = m_b r_b (=C)$$

whereby C is a field dependent constant. Dimensionless numerical equivalent relation $m_a/m_b = r_b/r_a$ suffices for recoil corrections. The underlying classical universal relations between m_x and r_x are

$$m_x = C/r_x \text{ or } r_x/C = 1/m_x.$$

If separation r_{HH} required addition, reduced mass μ appears naturally, since

$$r_{HH} = (r_a + r_b) = C(1/m_a + 1/m_b) = C(m_a + m_b)/(m_a m_b) = C/\mu$$

Similarly, if total mass m_{HH} required addition, reduced separation $\varrho = r_a r_b / (r_a + r_b)$ appears naturally too, since

$$m_{HH} = m_a + m_b = C(1/r_a + 1/r_b) = C(r_a + r_b)/(r_a r_b) = C/\varrho$$

This explains the difficulties above with (4c), the classical result for r_{HH} , since $\varrho = \frac{1}{2}r_{HH}$ for H_2 .

If the *sum-based* reduced separation is ϱ_+ , a *difference-based* reduced separation ϱ_- obeys

$$1/\varrho_- = 1/r_a - 1/r_b = (r_b - r_a)/r_a r_b$$

which appears in (6f).

Field dependent C obeys classically $C_f = e^2/v^2 = (e^2/c^2)/\alpha^n$, with unit charge e , velocity of light c and fine structure constant α . Values $n=0, 1$ and 2 typify different interactions: $n=0$ for strong (e^2/r_0), $n=1$ for weaker electromagnetic, Compton-de Broglie ($\alpha e^2/r_0$) and $n=2$ for even weaker Coulomb interactions ($\alpha^2 e^2/r_0$) in atom H

instead of linear qv in Dunham's (6d). The reduced Kratzer oscillator difference is now

$$\Delta V_{SK}^{'} = -\frac{1}{2}[1 - qv / (1 - \frac{1}{4}q^2v^2)]^2 + \frac{1}{2} = +qv / (1 - \frac{1}{4}q^2v^2) - \frac{1}{2}q^2v^2 / (1 - \frac{1}{4}q^2v^2)^2 \quad (6h)$$

to be compared with Dunham's (6d). In cm^{-1} , the numerical Kratzer result is

$$\Delta V_{SK} = (+4410,17v - 123,34v^2 - 3,49v^3) / (1 - 0,00078v^2)^2 \text{ cm}^{-1} \quad (6i)$$

as it entails naturally and from first principles only, higher order terms in v as suggested by (1b)-(1c). Analytical Kratzer result (6i) is a further improvement for (1a). Unlike (6c), a parameter for qv in (6g) can affect the goodness of fits (see below). As for (6e), also (6i) is an analytical first principles formula of closed form, based solely on m_H as input for the complete H_2 spectrum.

V.2 Results with achiral Dunham and Kratzer bond theories

Since optimization is also used in QM, using a parameter for qv is allowed. Multiplicative⁹ or external parameters p_e cannot improve the goodness of a fit, since size does not affect classical Euclidean symmetries (ratio's, proportions). However, internal parameters p_i affect (dynamic) symmetries. In parameterized HO $[p_e(x_1 - p_i x_2)]^2$, the position of the extreme is not affected by p_e but it is by p_i . Whereas external p_e cannot affect the goodness of a fit for a vibrator, internal p_i can. Typical *external scaling parameters* for bonds are Dunham's a_0 , fundamental frequency ω_e , bond energy D_e , all in cm^{-1} , if energy $E(r)$ is in cm^{-1} . Non-dimensionalization with *external multiplicative scaling* parameters only gives variables, commensurate with scaling parameters. *Internal parameters* can determine the goodness of a fit as they refer to *internal or dynamical symmetries*.

To normalize results, we compare variable qv or Dunham's δ_{HO} (for which parameterization is ineffective), with parameterized Kratzer's δ_{SK}/p (p being an internal parameter p_i) using

$$(i) \quad \delta_{HO} = qv \quad (7a)$$

$$(ii) \quad \delta_{SK}/p = (1/p)[1/(1 - \frac{1}{2}pqv) - 1/(1 + \frac{1}{2}pqv)] = qv / (1 - \frac{1}{4}p^2q^2v^2) \quad (7b)$$

This secures leading term qv is identical for all 14 vibrational levels v in *either method*. The main difference between the 2 resides in normalizing factors: 1 for Dunham's but $1/(1 - \frac{1}{4}p^2q^2v^2)$ for Kratzer's potential, although critical points can emerge because of $1/(1 - \frac{1}{2}pqv)$. Normalizing Kratzer's potential as in (7b) brings in *harmonic mean* $[(1 - \frac{1}{2}pqv)(1 + \frac{1}{2}pqv)] = (1 - \frac{1}{4}p^2q^2v^2)$, a more natural feature to discuss a *harmonic* oscillator.

The accuracy of the 2nd order fit with Kratzer's variable (7b) is maximum for $p = p_i = 0,83795$.

The 2nd order fits for plots of levels versus δ_{HO} (7a) and $\delta_{SK}/0,83795$ (7b) in Fig. 2 are respectively

$$E_{\delta(HO)} = -40971,3574\delta_{HO}^2 + 78614,1312\delta_{HO} - 161,1126 \text{ cm}^{-1} \quad (7c)$$

with a goodness of fit $R^2 = 0,9998627$ and

⁹ QM parameterization is typically multiplicative or external. This was criticized in the EPR-paper [30] on the completeness of QM: additive scaling affects the symmetry-effects associated with variables, as shown here.

$$E_{\delta(\text{SK})} = -40754,1814\delta_{\text{SK}}^2 + 76766,2419\delta_{\text{SK}} - 3,56576 \text{ cm}^{-1} \quad (7d)$$

with a much better goodness of fit $R^2=0,9999999$.

Although coefficients in (7c) and (7d) are comparable with values as theoretically expected, their difference clearly shows in Fig. 3, where errors of (7c) and (7d) in Table 2 are plotted versus v . Errors of 3 cm^{-1} or $0,021 \%^{10}$ for (7d) almost vanish when compared with those for (7c), since they are 30 times smaller than for Dunham's (7c), which are 111 cm^{-1} or $0,54 \%$. They are 530 times better than HO recipe (1a) with its errors of 1840 cm^{-1} (see Section II).

Moreover, Kratzer's simple 2nd order parabola is even more accurate than a 4th order fit in v for (1c), i.e. a Dunham quartic, since this gives errors of 7 cm^{-1} , see Table 2. A 4th order Dunham oscillator has the 3 terms in d_D^2 , d_D^3 and d_D^4 in (2c), whereby the latter two relate to Varshni's F and G (see Section I). We return to this problem in the Discussion (Section VI).

A 4th order fit with Kratzer's variable (7b) is, however, not significantly better (not shown). This is surprising, as chiral systems obey a Hund-type double well curve (a quartic) to separate the chiral constituents [31,32]. If H_2 was chiral or *asymmetric or less symmetric* instead of achiral as with (6b), *left-right asymmetries* must be found, a symmetry problem, discussed in [21].

Here, we discuss a last but very important problem: how to assess analytically the H_2 *covalent* bond energy D_e on the basis of an *ionic* Kratzer potential.

V.3 Covalent H_2 bond energy from an ionic Kratzer potential

Oscillator $D(1-x)^2$ and oscillator difference $D(1-(1-x)^2)=D(2x-x^2)$ in x transform respectively in $D((1-x')-1)^2=Dx'^2$ and $D[(1-x')^2-2(1-x')]$ with complementary¹¹ $x'=1-x$. In the latter case, the plot versus x' gives well-depth D as an intercept at $x'=0$, since, analytically, the linear term *has vanished* using a complementary variable¹¹. Although Coulomb's $-e^2/r$ vanishes exactly *by this complementary variable*, one cannot conclude that the system is not of Coulomb-type or not ionic. In fact, this is a *trompe-l'oeil* [2]: *first order Coulomb term $-e^2/r$, essential to get at a stable Coulomb system, is probed exactly by its absence.*

For the better performing Kratzer potential (7d) for H_2 , its first derivative $d/d\delta_{\text{SK}}$ (or $d/d\delta$ after dropping the suffix) gives extreme

$$\delta_{\text{max}} = 0,9418204$$

The maximum well depth, i.e. the *covalent bond energy* D_e of H_2 , is therefore

$$D_e = 36146,442 \text{ cm}^{-1}$$

¹⁰ Including atom energies (1 Hartree) and covalent D_e (sum 246500 cm^{-1}), % errors are *artificially* reduced to 0,0015. In practice and for the 14 bands between ~ 90000 and $\sim 55000 \text{ cm}^{-1}$ [12], errors reduce to only 0,011 % (not shown).

¹¹ However important, we do not expand on complementarity, where unit +1 consists of 2 complementary parts, e.g. $+1 = +x + (1-x)$. This equation is absolutely valid in whatever way x is defined. Unfortunately, any value of x will do and the equation remains useless, if not trivial, until extra constraints can be imposed, like those used below.

Complementary unit $+1=+x+1-x$ is now $+\delta_{\max}=\delta+\delta_{\max}-\delta$. Scaling with $\delta_{\max}=0,9418204$ gives a complementary unit description in Kratzer variable δ , applicable for H_2

$$+1 = p_e \delta + 1 - p_e \delta = 1,061773521\delta + 1 - 1,061773521\delta$$

External parameter $p_e=1/\delta_{\max}$ makes first order Coulomb term vanish exactly. Fig. 4 shows level energies plotted versus variables $x=p_e\delta$ and $x'=(1-x)=(1-p_e\delta)$. The 2nd order fits are respectively

$$E_x = -36150,0077x^2 + 72300,0154x - 3,5658 \text{ cm}^{-1} \quad (8a)$$

wherein $72300,0154 \approx 2 \cdot 36150,0077$ as required and

$$E_{x'} = -36150,0077x'^2 + 0,0000x' + 36146,4419 \text{ cm}^{-1} \quad (8b)$$

both giving the same small errors for Kratzer's parabola as in Table 2. *Ionic Kratzer potential* (8b) returns coefficient $36150,01 \text{ cm}^{-1}$ and intercept $D_e=36146,44 \text{ cm}^{-1}$, within 0,078 % of observed H_2 bond energy $D_e=36118,3 \text{ cm}^{-1}$ (without zero point energy [28]).

This simple, straightforward and fairly accurate result is only possible with an *ionic* Coulomb law at work in *covalent* H_2 using *harmonic* and *quantized* Sommerfeld-Kratzer potential (7c). For all levels E_v and D_e , these are the best results possible with a classical ionic Kratzer-Coulomb bond theory for *achiral* H_2 of the same first principle's status as Bohr H theory. They are better than with HO recipe (1a) and than with the first wave mechanical procedure¹² [33].

V.4 Formal connection with Bohr H theory

When compared with (1a), an advantage of (8b) is that average $36148 = \frac{1}{2}(36150+36146)$ gives

$$E_{x'} \approx 36148(1-x'^2) = D_e(1-x'^2) \text{ cm}^{-1} \quad (8d)$$

as simplified *ionic* Kratzer band equation, with asymptote *covalent* D_e , for a *complete molecular band spectrum* (H_2) based on quantization in v . This equation is formally similar to Bohr's

$$E_n = R_H(1-1/n^2) \text{ cm}^{-1} \quad (8e)$$

for a *complete line spectrum* (H Lyman series), with Rydberg R_H , based on quantization in n [34].

These equations show why simple ionic Kratzer bond theory can make covalent molecule H_2 prototypical for molecular spectroscopy, just like simple Bohr theory made atom H prototypical for atom spectroscopy (see Introduction).

VI. Discussion and prospects

(i) Kratzer Coulomb energy $-e^2/r_0$ is important for universal behavior and the UF [2,23]. Scaling by *ionic bond energy* D_{ion} , rather than *covalent* D_e [7,23] unifies the spectroscopic constants of *ionic and covalent bonds* between *all monovalent atoms in the Table* [2,23,35]. This representative qualifies for studying universal behavior [2,23]. For *covalent dimers* only, Varshni argued that a low parameter

¹² Heitler and London obtained less accurate $r_0=0,80 \text{ \AA}$, $\omega_e=4800 \text{ cm}^{-1}$ and $D=3,14 \text{ eV}$ or 25300 cm^{-1} [33].

UF is unlikely [7]. Comparing [35] with [6,7] shows that probing universal behavior depends on the bond set, which must be representative as well as physically meaningful [23]. Difficulties may point to defects of Dunham theory, as reflected in the constants scaled without using D_e [36]. Given their importance, UF-claims must be analyzed carefully. Self-contradictory claims must be falsified, e.g. by *reductio ad absurdum* [23].

(ii) The fact that *ionic bond energy* D_{ion} can be a better scaling aid [2,23,35] than *covalent* D_e has now been rationalized with an analytical relation between D_{ion} and D_e (see Sections V.4-5).

(iii) Universal behavior is usually connected with the smooth G(F)-plot of functions F for α_e and G for $\omega_e x_e$, whereby F and G relate to Dunham coefficients a_1 and a_2 in (2c) and to variable r/r_0 . With a Kratzer parabola in r_0/r , higher order terms are superfluous; higher order terms in v are only generated by the connection between v and r_0/r as in (6i). With (4d)-(4e), quadratic Kratzer term $\frac{1}{2}(e^2/r_0)(\omega_e/a_0)^2 = 0,5*4410,17^2/78844,91 = 123,34 \text{ cm}^{-1}$ is in agreement with observed H_2 levels. This Kratzer 2nd order term is close to H_2 anharmonicity $\omega_e x_e$ of $123,07 \text{ cm}^{-1}$ [6,12,25] in Dunham theory, where it is related to the 4th order term with coefficient a_2 .

(iv) Whereas Morse and Dunham oscillators are used more widely¹³ than Kratzer's [2], we proved why the interest in Kratzer's function [7,8,13,37]¹⁴ is justified. Performances of Morse-Dunham-Kratzer and Coulomb oscillators should be compared in more detail than hitherto.

(v) A recent double photoionization study [38] confirms the importance of non-Heitler-London, e.g. *ionic states*, for the H_2 ground state, which is exactly the result of *ionic* Kratzer bond theory [39]. Results [38] are theoretically modeled according to achiral recipe (6b), also used here.

(vi) For isotopomers HD, $D_2 \dots$ results must be as accurate as for H_2 , since, even in simple approximation $m_D = 2m_H$, similar r_0 values are obtained for D_2 . This suffices to extend the same ionic analysis above to these covalent isotopomers⁵ [25,27], without having to give details here.

(vii) For the connection with the fundamental constants, Section IV.1 revealed that, with (3g) and (3o), *radial velocity* in H_2 is $v = (1/f)e^2/h \text{ cm/s}$ or $e^2/h \text{ cm/s}$ for $f=1$, independent of m_H and r_0 . Scaling by c and taking c , e and h from [26] gives number

$$v/c = e^2/(hc) = 0,00116141 = 1/861,02258 = \alpha/(2\pi) \quad (9a)$$

which is exactly 2π times the inverse of Sommerfeld's fine structure constant $1/\alpha = 137,0359997$ [26] (see above) but also the Schwinger term for atom H in the context of QED (itself close to the anomaly for the electron's magnetic, not to be discussed here).

With (3c), the fundamental frequency (inverse time) for *periodical radial motion* in H_2 is

$$\omega = v/r_0 = \alpha c / (2\pi r_0) \text{ s}^{-1} \quad (9b)$$

In cm^{-1} , this analytical first principles result is

¹³ The number of citations to Kratzer's potential is only a fraction of those to Morse and Dunham potentials.

¹⁴ Applications of Kratzer's potential to other fields, e.g. nuclear physics, are not discussed here.

$$\omega'=\omega/c=\alpha/(2\pi r_0)=157689,8\text{ cm}^{-1} \quad (9c)$$

but this is exactly the *ionic bond energy* $D_{\text{ion}}=e^2/r_0=157689,8\text{ cm}^{-1}$ for H_2 , conform the r_0 value, derived from m_{H} (see Section IV.2), and so important for scaling, see points (i)-(iii).

(viii) Despite the good performances of an *ionic* Kratzer-Coulomb oscillator for *covalent* H_2 , % errors of 0,0015 or 0,021 (pending the method¹⁵) are not of spectroscopic accuracy¹⁵ and less precise than those of elaborate QM calculations [3]. However, Kratzer theory needs only one *parameter* for optimization, i.e. $p_i=0,83795$ for (7b), whereas [3] needs not less than 5. Kratzer theory gives acceptable results without a wave equation, whereas [3] needs hundreds of terms in the wave function of the simplest bond of all, H_2 . This illustrates some of the many conceptual and computational advantages of Kratzer-oscillator bond theory¹⁶. In [21], a parameter-free chiral Kratzer bond theory is presented, as accurate as [3] and within the errors of [12].

VII. Conclusion

Despite the difficulties in the Introduction, a fairly accurate simple bond theory exists, which is in line with a UF, the *Holy Grail of Molecular Spectroscopy* [2,9]. This classical *ab initio ionic* Kratzer bond theory, based on Bohr's old quantum H theory, is validated with fairly accurate vibrational levels for *covalent* bond H_2 , modeled as *an achiral system*. The theory gives an analytic connection between *ionic and covalent bond energies*. A main advantage is that only hydrogen mass m_{H} is needed as input to assess all H_2 vibrational levels. This unprecedented result justifies a search for *a more accurate, less symmetrical or chiral, ionic Kratzer bond theory*, which we present in [21].

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¹⁵ Observation [12] gives errors for H_2 quanta of $0,1\text{ cm}^{-1}$ [40] or 3000 MHz, much larger than errors for H lines [34].

¹⁶ To the best of my knowledge, no simpler, better molecular potential of 2nd order in a single variable can be found.

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Table 1. Observed vibrational levels for H₂ [12] (in cm⁻¹)

v	quanta	levels
0	4401,21	0,00
1	4161,14	4161,14
2	3925,79	8086,93
3	3695,43	11782,36
4	3467,95	15250,31
5	3241,61	18491,92
6	3013,86	21505,78
7	2782,13	24287,91
8	2543,25	26831,16
9	2292,93	29124,09
10	2026,38	31150,47
11	1736,66	32887,13
12	1415,07	34302,20
13	1049,16	35351,36
14	622,02	35973,38

Table 2 Errors for H₂ levels with Dunham (2nd and 4th order) and Kratzer (2nd order) functions (in cm⁻¹)

v	levels	Dunham		Kratzer
		2 nd order	4 th order	2 nd order
0	0,00	161,11	8,08	3,57
1	4161,14	53,18	-8,34	-3,91
2	8086,93	-33,74	-8,43	-3,94
3	11782,36	-94,63	-1,67	-0,77
4	15250,31	-126,64	5,20	2,45
5	18491,92	-128,61	8,56	4,15
6	21505,78	-101,96	7,09	3,59
7	24287,91	-50,66	1,75	1,13
8	26831,16	18,13	-4,81	-2,02
9	29124,09	92,98	-9,39	-4,48
10	31150,47	157,65	-8,71	-4,51
11	32887,13	188,98	-1,59	-1,37
12	34302,20	155,08	9,30	4,04
13	35351,36	11,66	13,69	6,80
14	35973,38	-302,54	-10,72	-4,73
	% error	0,536	0,044	0,021

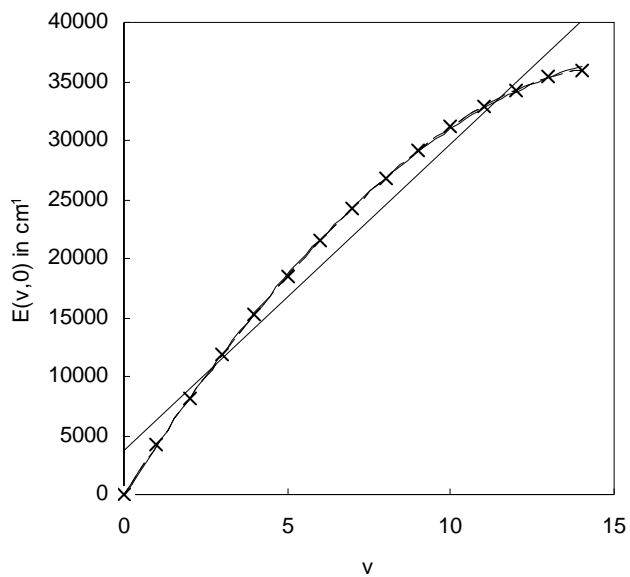


Fig. 1 Plot of 14 vibrational levels $E(v,0)$ versus v [12].
Linear fit (full line); 2nd, 4th and 6th order fits coalesce to a single broad curve (dashes).

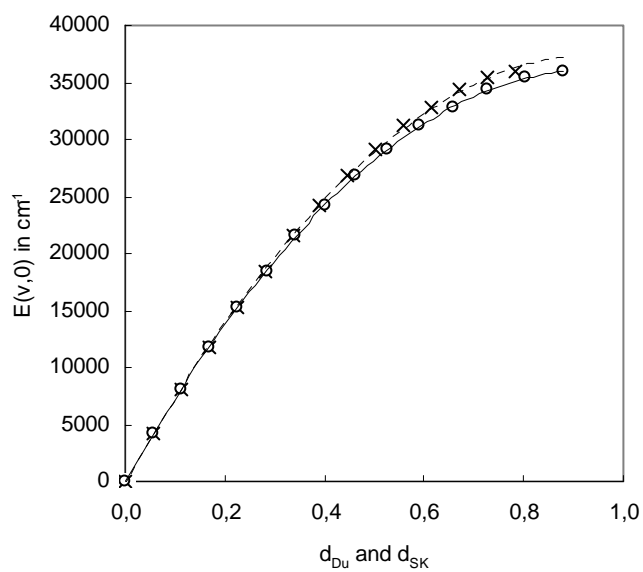


Fig. 2 Plot of $E(v,0)$ versus d_{DU} (dashes) and d_{SK} (full) for 2nd order fits

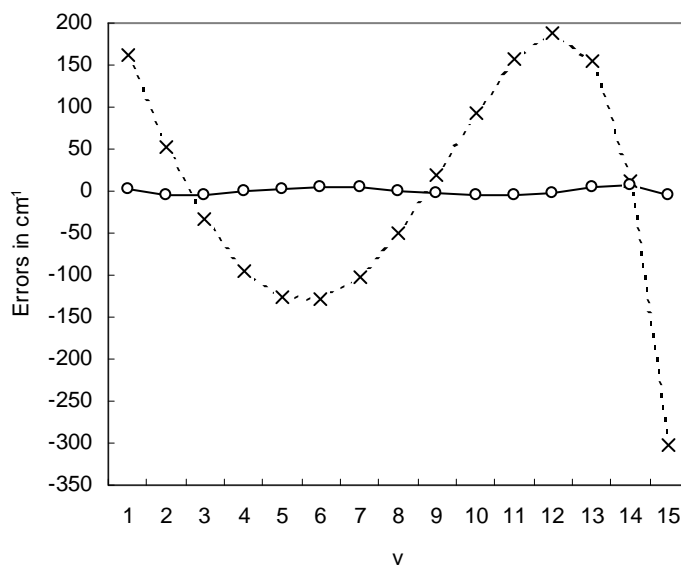


Fig. 3 Errors with 2nd order fits for Dunham (x) and Kratzer (o) oscillators.

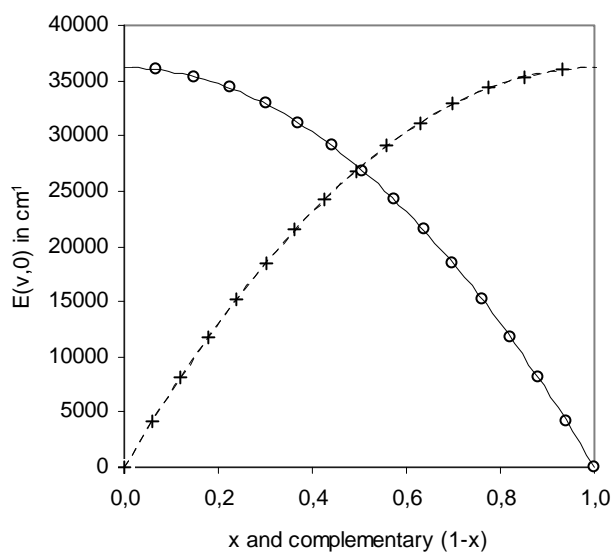


Fig. 4 Energy levels with Kratzer parabola (8a) versus x (+, dashes) and (8b) versus complementary 1-x (o, full line), giving D_e as intercept (see text)