

THE ARCHITECTURE OF DIATOMIC MOLECULES

**PART II: STUDY OF HYDROGEN MOLECULE'S
ELECTRONIC VIBRATIONAL DATA**

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ABSTRACT

In Part I of this work, we established that, the *vibration period* T of a diatomic molecule, can be expressed as $T = [4\pi^2 / (\sqrt{n_1 n_2} h)] \sqrt{g M_0 m_e} r^2$, where M_0 is the *reduced mass* of the nuclei, m_e the *mass of the electron*, r the *internuclear distance* of the molecule at the given electronic state, h the *Planck Constant*, and g a *dimensionless and relativistically invariant coefficient*, which appears to be a *characteristic* of the *electronic configuration* of the molecule.

Herein, we will validate this relationship, chiefly on the basis of vibrational *data* of H_2 molecule's *electronic states*. This, basically yields, the *elucidation* of the *complete set* of H_2 *spectroscopic data*. The *composite quantum number* $n_1 n_2$ along our finding, is briefly speaking nothing but the ratio of the internuclear distance r at the given electronic state, to the internuclear distance r_0 at the ground state, provided that these two states are configured similarly.

This makes that for electronic states configured alike, for which g is expected to remain the same, T^2 versus r^3 , should exhibit a linear behaviour.

1. INTRODUCTION

Herein, we consider the spectroscopic data of H₂ molecule, i.e. *vibration frequency* ω , versus *internuclear distance* r , at *various electronic levels*, along the findings^{1,2} presented in Part I of this work. Note that ω is the inverse of the *vibrational period* T .

The data tabulated in Section 2, as expected, should *basically* agree with the *approximate empirical relationship*, $\omega r^2 = \text{Constant}$;^{3,4} it indeed does.

This relationship does not involve though, any *quantum numbers*.

We established a more correct relationship for the *vibrational period* T_0 :^{1,2}

$$T = \frac{4\pi^2}{h\sqrt{n_1 n_2}} \sqrt{g M_0 m_e} r^2 . \quad (1)$$

here, h is the *Planck Constant*; M_0 is the *reduced mass* of the molecule; m_e is the *electron mass*; g is a *dimensionless and relativistically invariant coefficient*, which we previously called the “*bond looseness factor*” (given that the inverse of it, is roughly proportional to the dissociation energy of the molecule); n_1 and n_2 are *principal quantum numbers* associated with the bond electrons; we have shown that the *composite quantum number* $n_1 n_2$, is merely the *ratio* of the internuclear distance r of the molecule at the given state, to the internuclear distance r_0 , it assumes at the ground state, provided that the two states are configured similarly.

In this article we will investigate Eq.(1), on the basis of H₂ molecule.

We thus expect that the plot T^2 versus r^3 behaves as a *straight line* passing by the origin for electronic states of H₂, configured similarly, for which g is expected to remain the same, for g is *purely* dependent on the *electronic structure* of the bond of concern.

This is considered in Section 3.

The reason we choose H₂ as a *prime basis*, is not only that this molecule is the simplest we can consider along Eq.(1), but it is the molecule on which the data regarding electronic states is the most abundant.

In Section 4, we try to elucidate data for which, g differs *evidently* from that associated with the majority.

We conclude in Section 5.

2. THE HYDROGEN MOLECULE SPECTROSCOPIC DATA: THE ELUCIDATION OF THE EMPIRICAL RELATIONSHIP $\omega r^2 = \text{CONSTANT}$

The hydrogen molecule, being the simplest diatomic molecule, its spectroscopic data should be carefully examined in order to check the *validity* of the theory we developed previously, and achieve its tuning.

We thus present in Table 1, the lowest *vibration frequency* ω versus the *internuclear distance* at various electronic levels, of hydrogen molecule.⁵

Along this, we should consider the relationship about the vibrational *period* i.e. Eq.(1) which we established, in regards to the *electronic states, lowest vibrational states*” of H₂ molecule. g , purely related to the “*electronic configuration characteristics*” of the molecule, is expected to remain fundamentally the same for energy levels configured similarly.

In Part I we have determined that the composite quantum number $n_1 n_2$ appearing in Eq.(1) is given by

$$n_1 n_2 = \frac{r}{r_0}, \quad (2)$$

where r_0 is the internuclear distance at the ground state, provided that the ground state and the electronic state of concern are configured similarly.

This suggests that, out of Eq.(1), we have

$$\omega r^2 \cong \text{Constant} \cong \frac{h}{4\pi^2 \sqrt{M_0 g m_e}}, \quad (3)$$

regarding electronic states involving internuclear distances close to each other, for which $n_1 n_2$ according to Eq.(2), turns out to be approximately *unity*.

This right away yields $\omega r^2 \cong \text{Constant}$, unveiling the *approximate empirical relationship* left in the dark, since about three quarters of a century,^{4,5} the approximate constant being that displayed by Eq.(3). Note that regarding the electronic states of a given molecule $M_0 m_e$, is a constant.

Through the inspection of Table 1, we see clearly that $\omega_0 r_0^2$, except for “*six data*” that we are to handle separately, stays indeed fairly *constant*, as predicted by Eq.(3); the *average* is $2455 \text{ cm}^{-1} \times \text{\AA}^2$, the *standard deviation* being around 5%.

The data presented in Table 1, can also be sketched as the period T ($1/\omega$) versus r^2 (Figure 1).

Table 1 Vibrational Electronic Data of Hydrogen Molecule ⁵

ω (cm ⁻¹)	r (Å)	ωr^2 (cm ⁻¹ Å ²)	Relative Error (%)	$\omega^2 r^3$ (cm ⁻² Å ³) x10 ⁻³	Relative Error (%)	Given Explanation
2225	1.072	2557	4.15	6099	4.5	(1s σ) (4f π)
2416	1.031	2570	4.68	6397	8.9	(1s σ) (5f σ)
2173	1.06	2441	0.57	5624	3.6	(1s σ) (5d σ)
2196	1.057	2454	0.04	5695	2.3	(1s σ) (5p π)
2457	0.96	2264	7.8	5341	9.	(1s σ) (4f σ)
2216	1.067	2521	2.7	5965	2.3	(1s σ) (4p π)
2140	1.062	2414	1.7	5485	6.2	(1s σ) (4p σ)
2088	1.83	6933		26719		[CsH ^T] [*]
2267	1.04	2452	0.12	5781	0.7	(1s σ) (3s σ)
2240	1.05	2440	0.61	5809	0.3	(1s σ) (3p π)
2064	1.107	2529	3.01	5779	0.8	(1s σ) (3p σ)
2522	0.989	2465	0.41	6153	5.3	(1s σ) (2s σ)
2342	1.038	2521	2.69	6134	5.	(1s σ) (2p π)
1983	1.38	3777		10334		[LiH ^T]
2176	1.6	5571		19395		[NaH ^T]
1835	1.8	5945		19638		[RbH ^T]
2142	1.06	2407	1.96	5465	6.6	(1s σ) (4d π)
2290	1.065	2597	5.78	6335	8.	(1s σ) (3s σ)
2325	1.034	2486	1.26	5976	2.5	(1s σ) (3p σ)
2220	1.077	2575	4.9	6157	5.4	(1s σ) (3d σ)
2108	1.059	2364	3.71	5278	10.4	(1s σ) (3d π)
2227	1.085	2622	6.8	6335	8.05	(1s σ) (3d σ)
2233	1.7	6445		24498		[KH ^T]
1000	2.32	5382		12487		(2p σ) (2p σ) [Li ₂ ^T]
2328	1.012	2383	2.93	5617	3.7	(1s σ) (2s σ)
2309	1.033	2464	0.37	5877	0.9	(1s σ) (2p π)
1317	1.293	2200	10.4	3749	55.4	(1s σ) (2p σ)
4168	0.742	2292	6.64	7097	18	(1s σ) (1s σ)

* Cf. Table 2, below.

Average of Unambiguous Data		2455	4.3	5825	7.6	
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3. PLOT OF T^2 VERSUS R^3

When we insert Eq.(2) into Eq.(1), we arrive at

$$T = \frac{4\pi^2 \sqrt{r_0}}{h} \sqrt{gM_0 m_e} r^{3/2}. \quad (4)$$

Thus for a given molecule, the plot of T^2 versus r^3 shall exhibit a linear behaviour, had g practically remained the same, for the electronic states in consideration.

Table 1 and the related Figure 2, indeed show that, for most of the excited states of H_2 molecule, T^2 versus r^3 behaves as a straight line, suggesting that g , for the *majority* of these states, can indeed be considered nearly constant.

In fact, one may ask how come that both $T \sim r^2$ and $T^2 \sim r^3$ behave as a straight line (*regarding the same data*), within close margins of scatters. The answer is that, based on Eqs.(1) and (2), for excited states with *close internuclear distances*, as we stated, $T \sim r^2$ is approximately a straight line. $T^2 \sim r^3$ is a more correct behaviour; but then apparently, the states in question do not exactly display the same electronic structure.

Through the inspection of Table 1, we see clearly that $\bar{\omega}^2 r^3$, except for mainly “*six data*” that we are to handle separately, stays indeed nearly *constant*, as predicted by Eq.(4); the *average* is $5825 \text{ cm}^{-2} \times \text{\AA}^3$, the *standard deviation*, still around 5%, if we do not take into account, the off line data corresponding to the state $(1s\sigma)(2p\sigma)$ (*displaying a standard deviation of 55%*).

Note that for H_2 molecule, the factor g can, through a perturbative Schrödinger analysis, be separately calculated to be 0.8, and this is perfectly justified by the RHS of Eq.(4), validating our theory from a totally different perspective.

We call the lined up data, “*unambiguous data*”.

There are yet data very much off the average straight line T^2 versus r^3 ; we call these “*ambiguous data*”, which as we shall see below, presumably delineate a different character than the majority, “*unambiguous datas*”.

4. THE AMBIGUOUS H₂ ELECTRONIC STATES ARE CONFIGURED JUST LIKE THE GROUND STATES OF ALKALI MOLECULES OR THOSE OF ALKALI HYDRIDES

Our raw relationship^{1,2}

$$T_0 \sim \frac{4\pi^2}{h} \sqrt{gM_0 m_e} r_0^2 \quad [\text{Eq.(14) of Part I}], \quad (5)$$

suggests that, amongst the hydrogen molecule electronic vibrational data, we should be able to identify *states, configured like alkali molecules or alkali hydrides' ground states*, by replacing the alkali molecule nuclei reduced mass, M_0^{Alkali} by the hydrogen molecule nuclei reduced mass, $M_0^{\text{H}_2}$.

A *change in the mass of the nuclei* indeed, does not practically affect the *electronic configuration* of the molecule.

However while reducing *hypothetically*, the mass of say Li₂ to the mass of H₂, on the basis of the above relationship, we do not *exactly* simulate the corresponding (2s)(2s) excited electronic state of H₂, since the *electronic configuration* of the *lighter fictitious end molecule* still bears the *electronic configuration* of Li₂, which is not quite the H₂ electronic configuration we aim at.

Nonetheless we anticipate that, this lighter *fictitious* Li₂ molecule (bearing H₂ molecule's mass) will still satisfactorily *delineate* the internuclear distance of the H₂ excited state, we aim to identify (*had this ever existed*).

The *internuclear distance* of Li₂ molecule is 2.67 Å, versus 2.32 Å, for the (2p)-(2p) bond, in H₂ molecule (cf. Table 1), and we shall promptly determine that this H₂ bond and the Li₂ *ground state bond*, are alike.

Thus, out of T_0^{Alkali} , the vibrational period of an *alkali hydride* or an *alkali molecule*, based on Eq.(5), we propose to calculate a transposed (“Trsp”) period, T_0^{Trsp} , such that

$$T_0^{\text{Trsp}} = T_0^{\text{Alkali}} \sqrt{\frac{M_0^{\text{H}_2}}{M_0^{\text{Alkali}}}}. \quad (6)$$

Accordingly, we expect T_0^{Trsp} to be satisfactorily close to the corresponding *datum* taking place amongst *hydrogen molecule spectroscopic data*. (We also expect that, the *internuclear distance* of the *original alkali base molecule*, is about the same as that of the H₂ molecule excited state, in question.)

Despite the *difference* between the *transposed datum* created via Eq.(4), and the corresponding H_2 *irregular datum*, the *conclusion* that the transposition in question yields, about the *verification of this latter*, looks rigorous.

This makes our approach, based on Eq.(6), an *efficient tool* toward the *identification* of H_2 *unambiguous data*.

Thence we produce Table 2, for T_0^{Trsp} [“T” is adopted to shorten “Trsp”], versus T_0^{E} [“E” standing for experimental], based on different *alkali molecules* and *alkali hydrides* (A), as well as the *data belonging to the hydrogen molecule* and *matching closely*, the results calculated out of Eq.(6). Figure 3 displays the square of the *calculated transposed data* with respect to *the cube of the internuclear distances* of the *alkali molecules* and *alkali hydrides*.

Within this context, note that (*as expected*) the “*relative error*” on the “*period*”, displayed at the last column of Table 2, is satisfactorily small, chiefly, for light alkali molecules, (*for which the bond electronic structure should be closer to that of the corresponding H_2 excited bond electronic structure*).

Likewise, for *alkali molecules* in consideration, we draw Table 3, showing the *measured internuclear distances of these molecules* (r_{0A}), and the *measured internuclear distances* (r_0) *of the excited electronic states of H_2* , bearing (*following our claim*), *electronic configurations similar to those of the ground states of alkali molecules*. The corresponding errors, together with the errors displayed by $\omega_0^2 r_0^3$ (cf. Table 1), are also sketched; the relatively small magnitude of these errors indicates indeed, a *satisfactory match*, in between the respective r_{0A} and r_0 quantities.

This is how we could come to identify the *ambiguous data* related to H_2 molecule, and draw Figure 4 (cf. also Table 1).

Let us emphasize that, although the “*transposition mechanism*” we visualized, does not exactly lead us to the *electronic configuration* of the excited H_2 *electronic state*; the *qualitative identification procedure* we draw seems to be quite *accurate*.

In short, the *ambiguous states seem to be configured like the corresponding alkali molecules’ ground states*.

This suggests that, the *ambiguous states* are located at higher energy levels than the others.

Furthermore H_2 *ambiguous electronic states* configured like *alkali-hydrides’ ground states*, seem to be configured asymmetrically, *whereas all H_2 unambiguous states seem to be configured nearly, like the ground state of H_2 molecule. (The H_2 ambiguous states configured like Li_2 , on the other hand, should be symmetrical.)*

Thus, on the contrary to what one would expect as a first approach, it appears that the H_2 bond configured like LiH ground state bond, is not really a $(1s\sigma)(2s\sigma)$ bond. This latter evidently exists (cf. Table 1), but the *related datum* evokes that the $(1s\sigma)(2s\sigma)$ bond is just like the H_2 ground state, quite *symmetrical* (*whereas the H_2 excited bond configured like LiH, should clearly be an asymmetrical bond*).

Table 2 The Measured Periods (T_0^E) of Different Excited States of H_2 , Configured Like Alkali Hydrides or Li_2 (in short, Alkali), in Comparison with the Calculated Periods (T_0^T), based on $T_0^T = T_0^{\text{Alkali Mol}} \sqrt{M_0^{H_2} / M_0^{\text{Alkali Mol}}}$, T_0^{Alkali} Being the Measured Period of the Alkali Hydride or Li_2 (in short, Alkali)

Identification Base	M_0 (Reduced Mass)	$T_{0H_2^*}$ ($\times 10^4$ c) [Exact Period of Irregular Excited (*) State of H_2]	T_0^E ($\times 10^4$ c) [Exact Period of Alkali Molecule (A)]	T_0^T ($\times 10^4$ c) (Transposed Period of A) [cf. Eq.(4)]	$\frac{T_0^T - T_{0H_2^*}}{T_0^T}$ $= -\frac{\Delta T_0}{T_0^T}$
Li_2	3.51	10.00	28.88	10.90	0.09
LiH	0.88	5.04	7.36	5.55	0.09
NaH	0.97	4.59	8.82	6.34	0.28
KH	0.98	4.48	10.56	7.47	0.40
RbH	0.99	5.45	11.0	7.82	0.30
CsH	1.00	4.79	11.55	8.17	0.41

Table 3 Error on the Internuclear Distances r_0 , of the Irregular States of H_2 Configured Like Alkali Hydride or Li_2 (in short, Alkali), and Error Displayed by $\omega_0 r_0^2$

Corresponding Molecule	ω_0 (cm^{-1}) (Exact Frequency Related to Irregular Data of H_2)	r_{0A} (\AA) (real)	r (\AA) of H_2	$\frac{r_{0A} - r_0}{r_{0A}}$ $= \frac{\Delta r_0}{r_{0A}}$	$\omega_0^2 r^3$ ($cm^{-2} \text{\AA}^3$)	$\frac{\Delta(\omega_0 r_0^2)}{\omega_0 r_0^2}$ $= -2 \frac{\Delta T_0}{T_0^T} + 3 \frac{\Delta r_0}{r_{0A}}$
Li_2	1000	2.67	2.32	0.13	1248.7	0.21
LiH	1983	1.59	1.38	0.13	1033.4	0.21
NaH	2176	1.89	1.6	0.15	1939.4	0.01
KH	2233	2.24	1.7	0.24	2449.7	0.08
RbH	1835	2.37	1.8	0.24	1963.7	0.12
CsH	2088	2.49	1.83	0.26	2671.8	0.04

Similarly, the H_2 bond configured like the NaH ground state bond seems to be not a $(1s\sigma)(3s\sigma)$ bond. This latter too evidently exists (cf. Table 1), but the *related datum* here again evokes that, the $(1s\sigma)(3s\sigma)$ bond too is, just like the H_2 ground state, quite *symmetrical*.

The same occurs for the bonds displayed by the H_2 excited levels, configured respectively like KH, RbH and CsH; thus these ought to be configured differently than the $(1s\sigma)(4s\sigma)$, $(1s\sigma)(5s\sigma)$, $(1s\sigma)(6s\sigma)$ H_2 bonds (sketched in Table 1).

CONCLUSION

The behaviour $T^2 \sim r^3$ can be successfully checked for the excited electronic states of other molecules, for which data is available. Note that the effort we developed along Eq.(6), could be extended, as well, to interpret the “*ambiguous data*” of other molecules. Thus, excited electronic states corresponding to such irregular data, lying at the RHS of the straight line about the period (T_0), versus the square of internuclear distance (r_0^2) (cf. Figure 1) (*drawn for the molecule in hand*), seem to be configured like, respectively, the *subsequential molecules’ ground states* (such as Li_2 , in regards to H_2), of the same chemical character.

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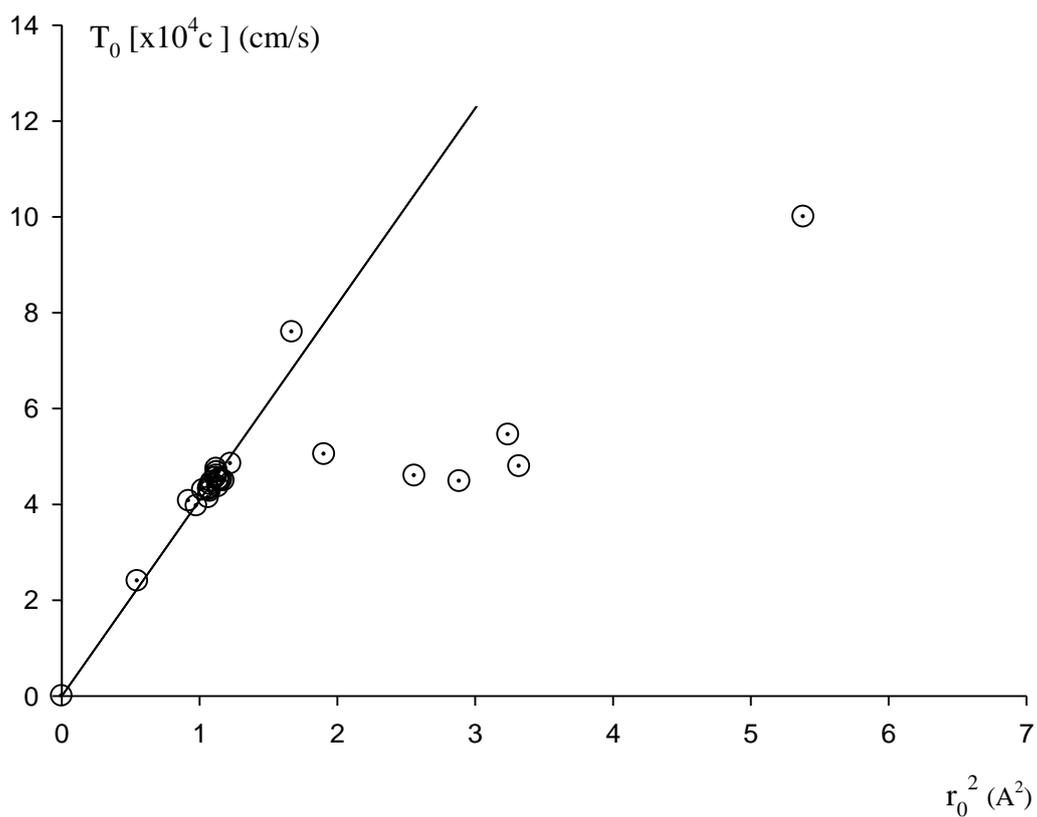


Figure 1 T_0 versus r_0^2 for different electronic states of H_2 based on experimental data

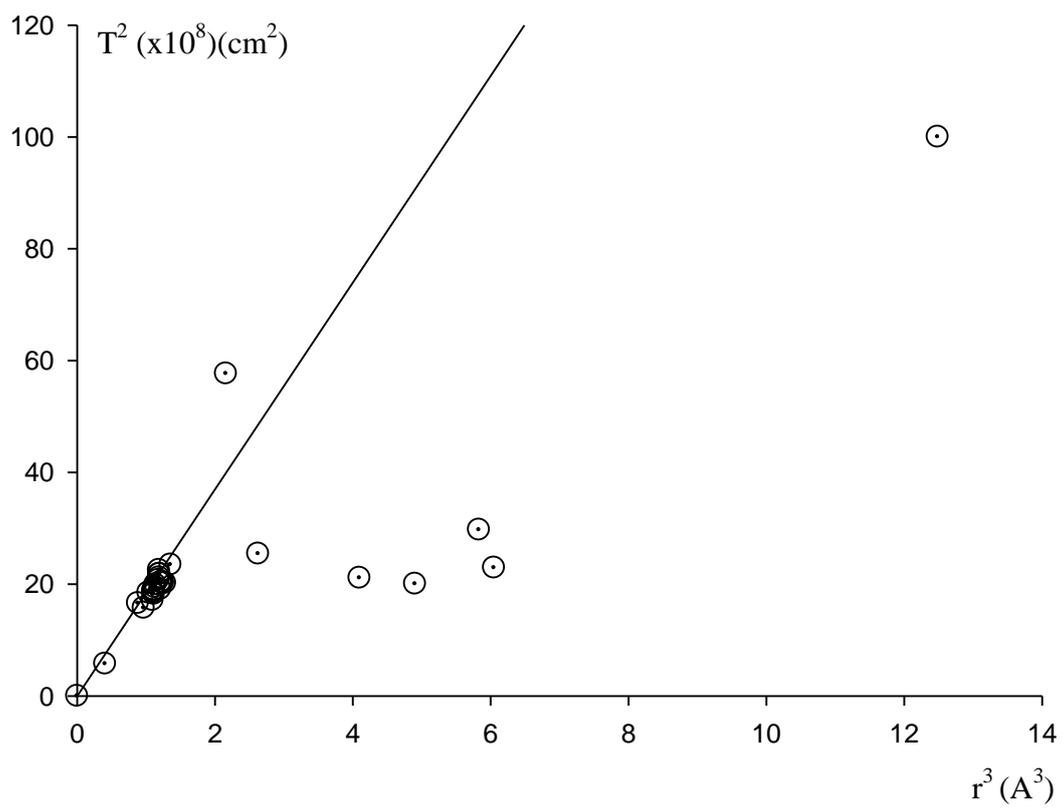


Figure 2 T^2 versus r^3 for different electronic states of H_2 based on experimental data

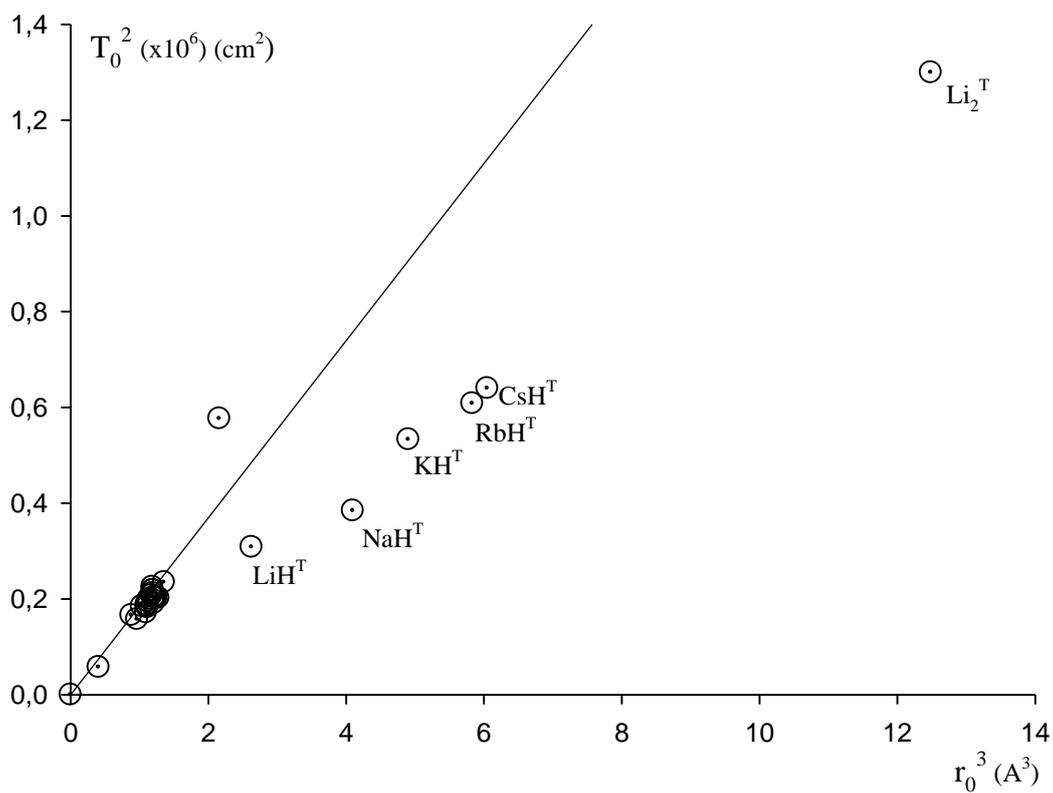


Figure 3 T^2 versus r^3 for different electronic states of H_2
 (For the states *off the straight line*, we calculate T_0 , on the basis of the *experimental period of alkali hydride* in question, or that of Li_2 , but using H_2 's *reduced mass*; we call this, the "*transposed period*" denominated by the superscript "^T".)

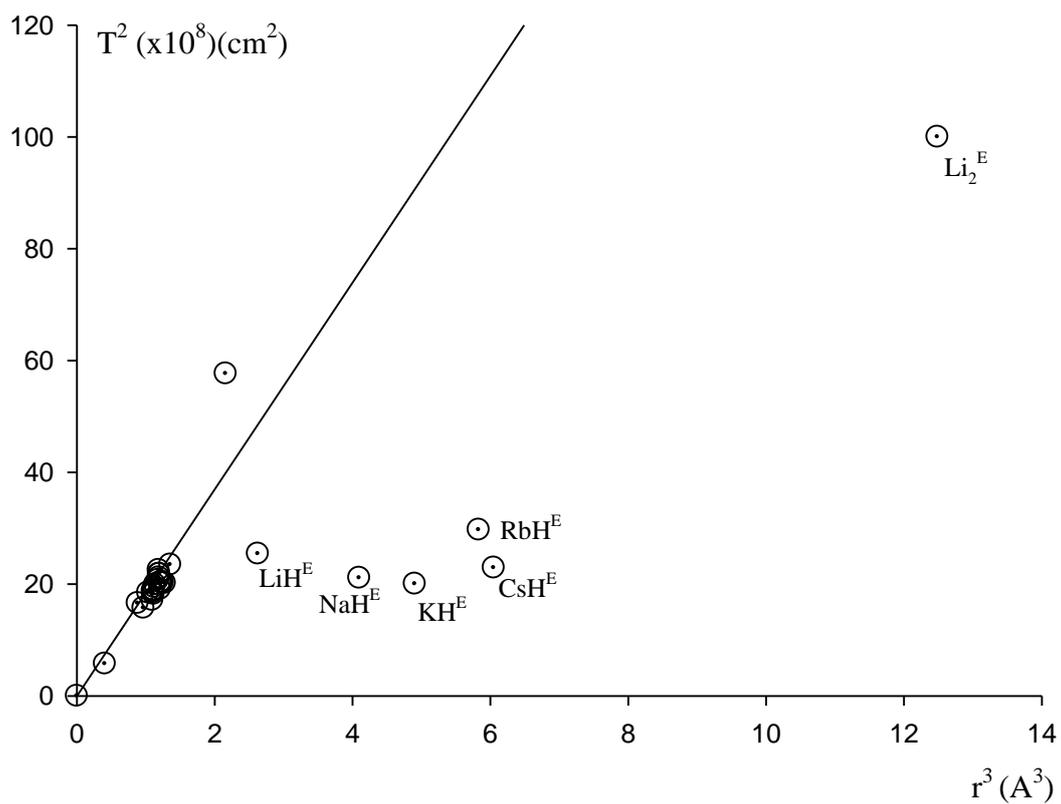


Figure 1 T^2 versus r^3 for different electronic states of H_2
 (The states corresponding to data *off the straight line*
 and denominated by the superscript "E" have been
 identified to be configured, as indicated, like the
 ground states of respectively, *alkali hydrides* and Li_2 .)

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