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Elucidation of the complete set of H_2 electronic states' vibrational data

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Received in revised form 24 December 2003; accepted 10 February 2004

Abstract

We have previously established that, the *vibration period T* of a diatomic molecule, can be expressed as $T = [4\pi^2/(\sqrt{n_i n_j}h)]\sqrt{g\mathcal{M}_0 m_e}r^2$, where $\mathcal{M}_0$ 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 validate this relationship, chiefly on the basis of *vibrational data* of H_2 molecule's *electronic states*, and achieve its *calibration*, vis-á-vis the *quantum numbers* that it is to involve. This, basically yields, the *elucidation* of the *complete set* of H_2 *spectroscopic data*. Thus, the composite quantum number $n_1 n_2$ along our finding is nothing but the ratio of the internuclear distance r at the given electronic state, to the internuclear distance r_0 at the ground state. 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 behavior*. Our approach can well be applied to other molecules.

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1. Introduction

Herein, we consider the spectroscopic data of H_2 molecule, i.e. *vibration frequency ω*, versus *internuclear distance r*, at *various electronic levels*, along our previous findings [1–5]. 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*, $\varpi r^2 \approx$ Constant [6,7]; it indeed does.

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

We established a more correct relationship for the *vibrational period T* [3,5]:

$$T = \frac{4\pi^2}{h\sqrt{n_1 n_2}}\sqrt{g\mathcal{M}_0 m_e}r^2, \tag{1}$$

here, h is the *Planck Constant*; $\mathcal{M}_0$ is the *reduced mass* of the molecule; m_e is the *electron mass*; g is a *dimensionless*

and relativistically invariant coefficient [3,5], it solely depends on the *electronic structure* of the bond; n_1 and n_2 are *quantum numbers associated with the bond electrons* [3,5]; we show 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, at the ground state, if both states are configured alike, i.e. [5,8]

$$n_1 n_2 = \frac{r}{r_0}. \tag{2}$$

In Section 3 we will investigate Eq. (1) considered together with Eq. (2), on the basis of H_2 molecule.

We thus expect that essentially the plot T^2 *versus r^3* behaves as a *straight line* passing by the origin for electronic states of any given molecule, provided that these states are configured similarly, so that g remains the same.

In Section 4 we clear out the data off the straight line, for which g evidently differs.

Note that our approach is a general one, and remains valid regarding the excited electronic states of any molecule.

One can further show that it holds well for the ground states of molecules belonging to a given chemical family, for which too, g remains the same, though this aspect goes beyond the scope of this article.

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Table 1
Ground vibrational data of hydrogen molecule, at different electronic states [5]

$\omega(\text{cm}^{-1})$	$r(\text{Å})$	ωr^2 $(\text{cm}^{-1}\ \text{A}^2)$	Relative error (%)	$\omega^2 r^3$ $(\text{cm}^{-2}\ \text{A}^3) \times 10^{-3}$	Relative error (%)	Explanation
2225	1.072	2557	4.15	6099	4.5	$(1s\sigma)(4f\pi)$
2416	1.031	2570	4.68	6397	8.9	$(1s\sigma)(5f\sigma)$
2173	1.06	2441	0.57	5624	3.6	$(1s\sigma)(5d\sigma)$
2196	1.057	2454	0.04	5695	2.3	$(1s\sigma)(5p\pi)$
2457	0.96	2264	7.8	5341	9.	$(1s\sigma)(4f\sigma)$
2216	1.067	2521	2.7	5965	2.4	$(1s\sigma)(4p\pi)$
2140	1.062	2414	1.7	5485	6.2	$(1s\sigma)(4p\sigma)$
2088	1.83	6933		26719		$[\text{CsH}^\text{T}]^\text{a}$
2267	1.04	2452	0.12	5781	0.75	$(1s\sigma)(3s\sigma)$
2240	1.05	2440	0.61	5809	0.3	$(1s\sigma)(3p\pi)$
2064	1.107	2529	3.01	5779	0.8	$(1s\sigma)(3p\sigma)$
2522	0.989	2465	0.41	6153	5.3	$(1s\sigma)(2s\sigma)$
2342	1.038	2521	2.69	6134	5.	$(1s\sigma)(2p\pi)$
1983	1.38	3777		10334		$[\text{LiH}^\text{T}]$
2176	1.6	5571		19395		$[\text{NaH}^\text{T}]$
1835	1.8	5945		19638		$[\text{RbH}^\text{T}]$
2142	1.06	2407	1.96	5465	6.6	$(1s\sigma)(4d\pi)$
2290	1.065	2597	5.78	6335	8.	$(1s\sigma)(3s\sigma)$
2325	1.034	2486	1.26	5976	2.5	$(1s\sigma)(3p\sigma)$
2220	1.077	2575	4.9	6157	5.4	$(1s\sigma)(3d\sigma)$
2108	1.059	2364	3.71	5278	10.4	$(1s\sigma)(3d\pi)$
2227	1.085	2622	6.8	6335	8.05	$(1s\sigma)(3d\sigma)$
2233	1.7	6445		24498		$[\text{KH}^\text{T}]$
1000	2.32	5382		12487		$(2p\sigma)(2p\sigma)$ $[\text{Li}_2^\text{T}]$
2328	1.012	2383	2.93	5617	3.7	$(1s\sigma)(2s\sigma)$
2309	1.033	2464	0.37	5870	0.9	$(1s\sigma)(2p\pi)$
1317	1.293	2200	10.4	3749	(55)	$(1s\sigma)(2p\sigma)$
4168	0.742	2292	6.64	7097	(35)	$(1s\sigma)(1s\sigma)$
Average of unambiguous		*2455*	*4.3*	*5285*	*~ 5*	

ᵃCf. Table 2, below.

2. The hydrogen molecule spectroscopic data: the elucidation of the empirical relationship $\varpi r^2 = \text{constant}$

3   The hydrogen molecule, being the simplest diatomic molecule, its spectroscopic data should be carefully ex-
5   amined in order to check the *validity* of the theory we developed previously, and achieve its tuning.
7   We thus present in Table 1, the *vibration frequency* versus the *internuclear distance* at various electronic levels, of
9   hydrogen molecule [9].

Along this, we should consider the *period relationship*
11   we established, i.e. Eq. (1), in regards to *ground vibrational states of different electronic states* of H_2 molecule.
13   Let us stress that *g*, being purely related to the "electronic *configuration characteristics*" of the molecule [5], is ex-
15   pected to be the same for *chemically alike molecules*. For the same reason, it should also remain fundamentally the
17   same, for energy levels configured similarly.

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

$$\varpi r^2 = \frac{h\sqrt{n_1 n_2}}{4\pi^2 \sqrt{\mathscr{M}_0 g m_\text{e}}}. \tag{3}$$

For electronic states involving internuclear distances close   19
to each other, $n_1 n_2$ via Eq. (2), turns out to be approximately
unity.   21

This right away yields $\varpi r^2 \approx$ Constant, deveiling the
approximate empirical relationship left in the dark, since   23
about three quarters of a century [6,7].

Note that regarding the electronic states of a given   25
molecule, $\mathscr{M}_0 m_\text{e}$ is virtually the same.

Let us now compare our guess with the data (presented   27
in Table 1).

Through the inspection of Table 1, we see clearly that   29
ϖr^2, except for "*six data*" that we call "*ambiguous data*",
and that we will have to handle separately, stays indeed   31
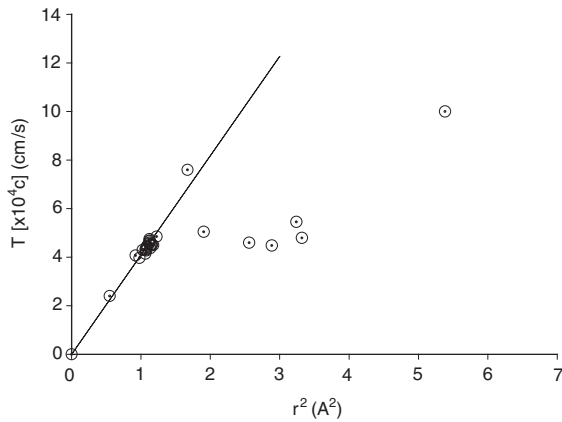approximately *constant*, as predicted by Eq. (3); the *average*

Fig. 1. T versus r^2 for different electronic states of H_2 based on experimental data.
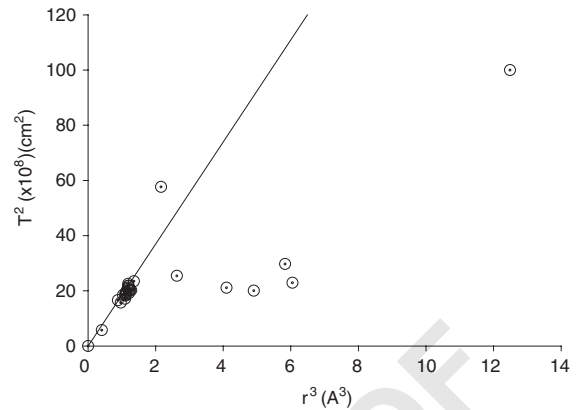

Fig. 2. T^2 versus r^3 for different electronic states of H_2 based on experimental data.

is 2455 cm^{-1} Å^2, the *standard deviation* being a little more than 4%.

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

3. Plot of T^2 versus R^3

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

$$T = \frac{4\pi^2\sqrt{r_0}}{h} \sqrt{g\mathcal{M}_0 m_e}\, r^{3/2}. \tag{4}$$

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

Table 1 and the related Fig. 2 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 $T-r^2$ and T^2-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, $T-r^2$ is only *approximately* a straight line. T^2-r^3 is a more correct behavior; 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 $\varpi^2 r^3$, except for mainly "*six data*", that we are to handle separately, stays indeed nearly *constant*, as predicted by Eq. (4); the *average* is 5285×10^3 cm^{-2} Å^3; the *standard deviation* is still around 5%, if we do not take into account, the off line data corresponding to the states $(1s\sigma)(1s\sigma)$ and $(1s\sigma)(2p\sigma)$ (*displaying a standard deviation about* 10 *times higher than the average*).

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, delineate a different *electronic configuration* than that delineated by the majority.

4. The ambiguous H_2 electronic states are configured just like the ground states of alkali molecules or those of alkali hydrides

Our raw relationship [1,2]

$$T_0 \sim \frac{4\pi^2}{h} \sqrt{g\mathcal{M}_0 m_e}\, r_0^2, \tag{5}$$

suggests that, amongst the *ground vibrational data of different electronic states*, *of the hydrogen molecule*, we should be able to identify *data* close to the *ground vibrational data of* respectively *alkali molecules or alkali hydrides*, via replacing the nuclei reduced mass, $\mathcal{M}_0^{\text{Alkali}}$ of the *alkali molecule* of concern, by the nuclei reduced mass, $\mathcal{M}_0^{H_2}$ of the hydrogen molecule. This should suggest that the electronic states of the *hydrogen molecule* in question are configured, just like the corresponding *alkali molecules or alkali hydrides*' ground states.

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 Li_2 to the mass of H_2, on the basis of the above relationship, we do not *exactly* simulate the corresponding $(2s)(2s)$ excited electronic state of H_2, since the *electronic configuration* of the *fictitious end molecule* is still the *electronic configuration* of Li_2, and is not *really* (*that of the corresponding* H_2 *excited electronic state*).

Nonetheless we anticipate that, this fictitious Li_2 molecule (bearing H_2 molecule's mass) will satisfactorily *delineate*

Table 2

The measured periods (T_0^E) of different activated 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 $T_0^T = T_0^{\text{alkali mol}} \sqrt{\mathscr{M}_0^{H_2} / \mathscr{M}_0^{\text{alkali mol}}}$

Identification base	$\mathscr{M}_0$ (Reduced mass)	$T_{H_2^*}(\times 10^4 c)$ (Exact period of ambiguous 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)]	$\dfrac{T_0^T - T_{H_2^*}}{T_0^T} = -\dfrac{\Delta T_0}{T_0^T}$
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

T_0^{alkali} being the measured period of the alkali hydride or Li_2 (in short, alkali).

the internuclear distance of the H_2 excited state (*had this ever existed*), we aim to identify. Indeed the *internuclear distance* of Li_2 molecule is 2.67Å, versus 2.32Å, for the (2p)–(2p) bond, in H_2 molecule (cf. Table 1), and we shall promptly determine that this *latter bond* and the Li_2 *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

$$T_0^{\text{Trsp}} = T_0^{\text{Alkali}} \sqrt{\frac{\mathscr{M}_0^{H_2}}{\mathscr{M}_0^{\text{Alkali}}}}. \qquad (6)$$

Accordingly, we expect T_0^{Trsp} to be satisfactorily close to the *datum* (*we have targeted*), taking place amongst *hydrogen molecule spectroscopic data.* We also expect that the *internuclear distance* of the *original base alkali molecule*, is about the same as that of the H_2 molecule *excited state*, in question.

Despite the *difference* between the *transposed datum* created via Eq. (6), and the corresponding H_2 *ambiguous datum*, the *conclusion, 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 *ambiguous 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). Fig. 2 displays the *calculated transposed data* with respect to *the square 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.*

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) *of the excited electronic states of* H_2, bearing (*following our claim*), *electronic configurations similar to those of the corresponding alkali molecules' states.* The *relative divergences* associated with r and $\omega^2 r^3$, respectively (cf. Table 1), are also sketched; the satisfactorily small magnitude of these divergences indicates indeed, a *fulfilling match*, in between the respective r_{0A} and r quantities.

This is how we could come to identify the *ambiguous experimental data* related to H_2 molecule, and draw Fig. 3 (cf. also Table 1).

In short, the *ambiguous states appear to be configured like the corresponding alkali molecules' ground states.* For this reason, we would like to call the H_2 "*ambiguous data*" of concern, "*alkali—like*" data (*and this qualitative conclusion is rigorous, although the transposition mechanism behind, does not lead us to the exact electronic configuration of the excited* H_2 *electronic state*).

Furthermore H_2 ambiguous electronic states configured like alkali-hydrides' ground states, should accordingly be configured asymmetrically (*whereas all of the* H_2 *unambiguous states seem to be configured like, practically, the ground state of* H_2 *molecule*).

The H_2 ambiguous state configured like Li_2, on the other hand, should obviously 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 $H_2(1s\sigma)(2s\sigma)$ bond is configured *nearly symmetrically*, just like the H_2 ground state (*whereas the* H_2 *excited bond configured like* LiH, *should clearly be an asymmetrical bond*).

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

Table 3
Error on the internuclear distances r, of the ambiguous states of H_2 configured like alkali hydride or Li_2 (in short, alkali), and error displayed by ϖr^2

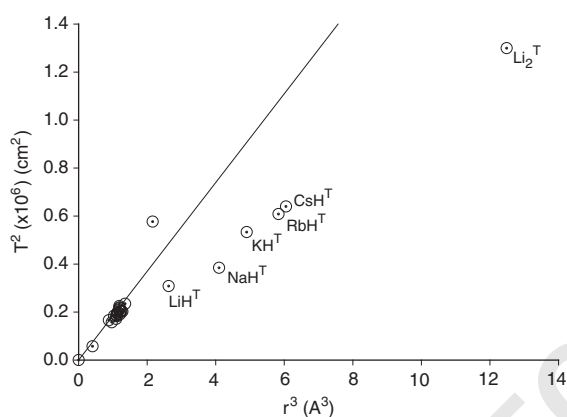| Corresponding molecule	$\varpi(cm^{-1})$ (Exact frequency related to ambiguous data of H_2)	$r_{0A}(\text{Å})$ (real)	$r(\text{Å})$ of H_2	$\dfrac{r_{0A} - r}{r_{0A}} = \dfrac{\Delta r_0}{r_{0A}}$	$\varpi^2 r^3$ ($cm^{-2}\ A^3$)	$\dfrac{\Delta(\varpi^2 r^3)}{\varpi^2 r^3} = -2\dfrac{\Delta T_0}{T_0^T} + 3\dfrac{\Delta r_0}{r_{0A}}$
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

Fig. 3. T^2 versus r^3 for different electronic states of H_2 (For the states *off the straight line*, we calculate T, 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 "*transpozed period*" denominated by the superscript "T".)

again evokes that, the $H_2(1s\sigma)(3s\sigma)$ bond too is configured *nearly symmetrically.*

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).

5. Conclusion

Herein we have elucidated the H_2 complete set of ground vibrational data, belonging to various electronic states.

The behavior T^2-r^3 can be successfully checked for the excited electronic states of other molecules, for which data is available. Furthermore 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 ambiguous data, lying at the RHS of the straight line about the period (T), versus the square of internuclear distance (r^2) (cf. Fig. 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 [10].

We would like to recall that, Eqs. (1) and (4) are *relativistically invariant.* This is deep; it means that, *space size, period of time,* and *mass* ought to be structured in just a given way, [3,5,11–14] and this is the one displayed by Eq. (5); thus the structure in question is imposed by the special theory of relativity. (What we mean by *mass* regarding diatomic molecules is $m_e\sqrt{\mathcal{M}_0/m_e}$, i.e. the *electronic mass* increased by the coefficient $\sqrt{\mathcal{M}_0/m_e}$.)

In fact, this is how we could arrive to the *transposition rule* expressed by Eq. (6).

It must be emphasized that, we encountered no work in the literature matching with the frame drawn herein.

On the other hand, based on the *comparison of the electronic energies* of the H_2 *excited bonds* configured like LiH, NaH, KH, CsH, RbH, and Li_2 (*which we like to call the ambiguous bonds*), with the *corresponding electronic energies* of the *ground states* of LiH, NaH, KH, CsH, RbH, and Li_2, yielding a *fine match*, respectively, one can conclude that the *ambiguous bonds* are indeed configured like the *corresponding alkali hydrides or molecules' ground states bonds*.

Note that the *dissociation energy of* H_2 *at the ground state* is greater than the *dissociation energy* of the *alkali hydride* LiH (*still at the ground state*), which is in return greater than the *dissociation energy* of the *alkali molecule* Li_2 (*still at the ground state*).

Accordingly, one can state that, the *dissociation energy of* H_2 *at the ground state* is greater than the *dissociation energy* of the H_2 *excited bond configured like* LiH, which is in return greater than the *dissociation energy of the* H_2 *excited bond configured like* Li_2, etc.

These facts may constitute interesting clues regarding the *dissociation process* of the hydrogen molecule at different excited states (*were they present*), vis-á-vis oxygen
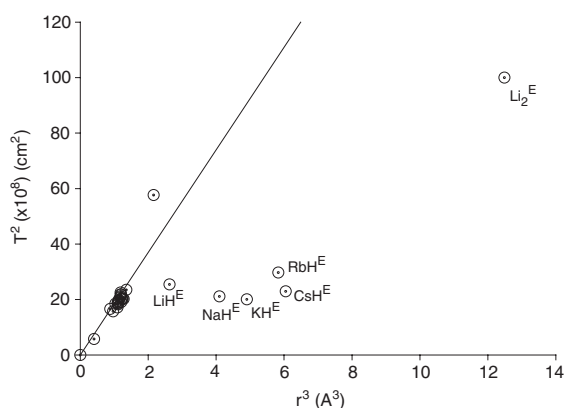
Fig. 4. T^2 versus r^3 for different electronic states of H_2. (The states corresponding to data *off the straight line* and denominated by the superscript "E" have been identified to be configured, as indicated, like the ground states of respectively, *alkali hydrides* and Li_2.)

molecules, in achieving a more efficient *burning* and *energy production* (Fig. 4).

Acknowledgements

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