Semi-empirical function of the dipole moment of LiH molecule

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In the framework of a semi-empirical method, the function of dipole moment of the LiH molecule in the ground electronic state has been derived in the form of a piecewise continuous function for the entire range of internuclear distances R. The function has a correct asymptotic behavior for both small and large R and coincides with the experimental one near the equilibrium internuclear distance R_e. The experimental value of the second derivative of the dipole moment function at the point R_e has been obtained, and the coefficient C_7 determining the behavior of the dipole moment function at large R as C_7/R^7 was found.

Introduction

According to the existing models of nuclear synthesis in the Big Bang, the first stars were formed of a gas consisting of light atoms: hydrogen, helium, and lithium. Then the simplest molecules like H_2 and LiH were formed of these atoms. The LiH molecule in large amounts is still present in the interstellar space and it is an object for active investigations in astrophysics. Most of these works were based on the measurements of absorption and emission spectra of the LiH molecules in space. This is favored by the fact that the LiH molecule has a large dipole moment, and therefore it actively participates in IR emission processes.

The dipole moment of the LiH molecule has been studied in many theoretical and experimental papers.[1–20] The experimental investigations yielded only the values of the dipole moment μ_e (see, e.g., Ref. 14) and its first derivative $\mu_e^{(1)}$ (Refs. 16 and 17) at the equilibrium internuclear distance R_e. With these values, the dipole moment function $\mu(R)$ can be determined only within a narrow range of internuclear distances R near R_e. In the theoretical papers,[1–4,18] the dipole moment functions $\mu(R)$ of the LiH molecule were calculated in a wider range of internuclear distances. However, the calculated functions $\mu(R)$ differ markedly at large R and no calculations are available for small R. Only one paper[17] is known, in which an attempt was undertaken to extrapolate the calculated dipole function from Ref. 18 into the range of small internuclear distances, but the obtained function $\mu(R)$ is strongly underestimated as compared to recent calculations.[1–4]

The aim of this work is to construct a semi-empirical dipole moment function of the LiH molecule for the entire range of internuclear distances.

Model dipole moment function

In Refs. 21–23, a semi-empirical method was proposed for the calculation of the dipole moment function of a diatomic molecule in the form of a piecewise continuous function consisting of three parts: $\mu(R)$ in the range of small internuclear distances R $(0 \le R \le R_1)$, including the vicinity of R_e; $\mu(R)$ in the range of moderate R $(R_1 \le R \le R_2)$, and $\mu(R)$ in the range of large R $(R_2 \le R < \infty)$. The dipole moment function in the range of large internuclear distances is modeled as a sum of the multipole and the exchange parts of $\mu(R)$. In the above cited papers, the dipole moment functions were calculated for hydrogen halides,[21] OH radical,[22] and for CO and NO molecules,[23] whose characteristic feature is that these molecules dissociate at $R \to \infty$ into atoms, at least one of which has its own quadrupole moment. In this case, the multipole part of the dipole moment function is caused by the dipole-quadrupole interaction operator and has the form C_4/R^4.

A characteristic feature of the LiH molecule is that at $R \to \infty$ it dissociates into the Li and H atoms in the ground states, which have no multipole moments. For this reason, the multipole part of the dipole moment function is determined in the second order of the perturbation theory and acquires the form C_7/R^7. With the allowance for this, the semi-empirical dipole moment function is defined as

$$\mu(R)=\begin{cases}\sum\limits_{i=3}^{n+3} a_i R^i, & 0 \le R \le R_1,\\ \sum\limits_{i=0}^{5} b_i R^i, & R_1 \le R \le R_2, \quad (1)\\ B_0 R^{\delta} \exp\left[-R\left(\beta^{\mathrm{Li}}+\beta^{\mathrm{H}}\right)\right]+\dfrac{C_7}{R^7}, & R_2 \le R < \infty.\end{cases}$$

Here, as in Refs. 21–23, the dipole moment function in the range of small R ($0 \le R \le R_1$) is determined in the polynomial form, which satisfies the condition $\mu(R) \sim R^3$ at $R \to 0$ and agrees with the dipole moment function in the form of the Taylor series in the vicinity of the point R_e:

$$\mu(R) = \sum_{i=0}^{n} M_i x^i, \qquad (2)$$

where $x = (R - R_e)/R_e$, and M_i are the coefficients, related to the dipole moment $\mu_e \equiv \mu_e^{(0)}$ and its derivatives $\mu_e^{(i)}$ as $M_i = \mu_e^{(i)}/i!$. Note that the number of the coefficients a_i in Eq. (1) coincides with the number of the known coefficients M_i and amounts to $n + 1$. The parameters β^{Li} and β^{H} of the dipole moment function in the range of large R ($R_2 \le R < \infty$) can be expressed through the ionization potentials $(\beta^{\mathrm{Li}})^2/2$ and $(\beta^{\mathrm{H}})^2/2$ of the Li and H atoms, while the parameter δ has the form $\delta = 2/\beta^{\mathrm{Li}} + 2/\beta^{\mathrm{H}} - 2/(\beta^{\mathrm{Li}} + \beta^{\mathrm{H}}) + 1$. The values of the parameters B_0 and C_7 can be found through fitting to the results of the *ab initio* calculations of the dipole moment function for the range of large R. The coefficients b_i are determined from the conditions of sewing together the dipole moment functions at small and large R accurate to second derivatives inclusive, and R_1 and R_2 are sewing points.

Calculation of the dipole moment function of the LiH molecule

According to this model, for the construction of the dipole moment function of the LiH molecule, it is necessary to know the constant C_7 and the derivatives of the dipole moment, and the number of these derivatives considerably influences the quality of the obtained dipole moment function. Note that the dipole moment functions for different isotopic modifications of the LiH molecule almost coincide (gravitational effects are negligibly small). In this paper, the dipole moment function was constructed with the use of the derivatives of the dipole moment of the main isotopic modification of the ^{7}LiH molecule.

Only the values of the constant dipole moment[14] and its first derivative[16,17] for the equilibrium position of molecular nuclei are now determined experimentally for different isotopic modifications of the LiH molecule. In addition, the dipole moments are determined for the ^{7}LiH molecule in the vibrational states $v = 0, 1, 2$; the ^{6}LiH and ^{6}LiD molecules in the vibrational states $v = 0, 1$; and the ^{7}LiD molecule in the ground vibrational state $v = 0$ (Refs. 13 and 14). These experimental data were used to calculate the second derivative of the dipole moment of the ^{7}LiH molecule by two methods. The first method involved the experimental values of the dipole moments of the ^{7}LiH molecule in the vibrational states $v = 0, 1$; while the second method involved the values of the dipole moments of the ^{7}LiH and ^{7}LiD molecules in the ground vibrational states.[14] In the calculations, the following equation for the dipole moment of the molecule in the vibrational state v was used:

$$\mu_v = \mu_e^{(0)} + \frac{1}{4}(-3a_1\mu_e^{(1)} + \mu_e^{(2)})(2v+1)(2B_e/\omega_e), \qquad (3)$$

where the Dunham coefficient a_1 was calculated as

$$a_1 = -\left[1 + \alpha_e\omega_e/(6B_e^2)\right]. \qquad (4)$$

The spectroscopic constants B_e, α_e, and ω_e were taken from Ref. 24, while the values of $\mu_e^{(0)}$ and $\mu_e^{(1)}$ were borrowed from Refs. 14 and 17 (Table 1). The determined second derivatives of the ^{7}LiH dipole moment are tabulated in Table 1.

Table 1. Experimental and theoretical values of the dipole moment (in D) of the ^{7}LiH molecule and its derivatives

μ_e	$\mu_e^{(1)}$	$\mu_e^{(2)}$	$\mu_e^{(3)}$
5.82775	3.238 ± 0.540[a]	2.00 ± 3.06[b]	
(Ref. 14)		1.20 ± 3.57[c]	
5.88711[d]	3.190[d]	1.80[d]	−12.5[d]
5.86506[e]	3.222[e]	1.77[e]	−11.7[e]
5.84831[f]	3.179[f]	1.88[f]	−14.1[f]
5.82887[g]	3.182[g]	1.83[g]	−13.3[g]

[a] Calculation using the experimental data from Ref. 7 with the use of μ_e from Ref. 14.

[b] Calculated with the use of experimental values of dipole moments of the ^{7}LiH molecule in the vibrational states $v = 0, 1$ [Ref. 14].

[c] Calculated with the use of experimental values of the dipole moments of the ^{7}LiH and ^{7}LiD molecules in the ground vibrational states [Ref. 14].

[d] Calculation with the use of theoretical data from Ref. 1.

[e] Calculation with the use of theoretical data from Ref. 2.

[f] Calculation with the use of theoretical data from Ref. 3.

[g] Calculation with the use of theoretical data from Ref. 4.

Note that the values of the second derivatives of the dipole moment presented well agree with each other, however the errors are too large.

The derivatives of the dipole moment were also calculated through the least-squares fit of the function $\mu(R)$ in the form (2) to the *ab initio* dipole moment function of the LiH molecule in the vicinity of the equilibrium position of the nuclei.[1–4] Thus obtained derivatives of the dipole moment $\mu_e^{(i)}$ ($i = 0$–3) are given in Table 1. It can be seen that the derivatives of the dipole moment determined from both theoretical calculations and experimental data are in a good agreement.

The parameters a_i, needed for calculating the dipole moment function of the LiH molecule in the range of small internuclear separations were determined with the aid of the coefficients M_0 from Ref. 14 and M_i (i = 1–7), determined from the data of *ab initio* calculations from Ref. 4 in the range $0.9 \le R \le 2.6$ Å. For the reasons that follow, the data from the Ref. 4 were taken as the basic ones. First, the number of experimental $\mu_e^{(i)}$ values is insufficient for good description of the dipole moment function of the LiH molecule in the range of small internuclear distances. Second, the theoretical values of $\mu_e^{(i)}$ from Ref. 4 are in a good agreement with the experimental data. In addition, as will be shown below, the function $\mu(R)$ from Ref. 4 has quite correct asymptotic behavior in the range of large internuclear distances.

The parameter C_7 was determined from the fit of the function $\mu(R) = C_7/R^7$ to the data of the *ab initio* calculations of the dipole moment function of the LiH molecule[4] at large internuclear distances ($R > 6$ Å). It is clearly seen from Fig. 1 that the results of *ab initio* calculations of $\mu(R)$ from Ref. 4 actually satisfy the C_7/R^7 dependence, which allowed the parameter C_7 to be estimated.

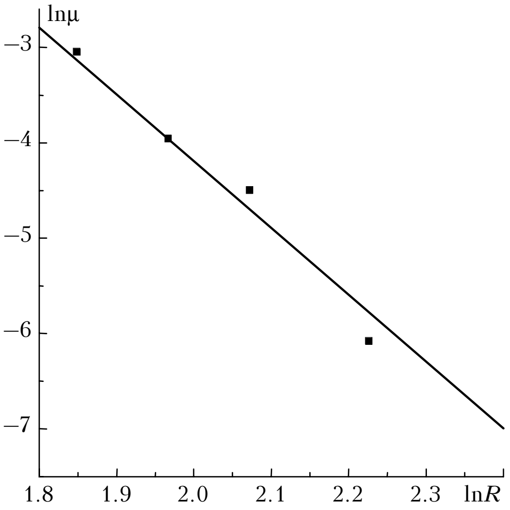

Fig. 1. Dipole moment function of the LiH molecule at large internuclear distances (R is measured in Å, μ is measured in D): $\ln\mu(R) = 9.8063 - 7\ln R$ function (solid line), *ab initio* calculation[4] (squares).

The determined value of the parameter C_7 is given in Table 2.

The parameter B_0 was determined with the use of the theoretical function $\mu(R)$ in the range $4.2 \le R \le 10.6$ Å from Ref. 4. The values of the parameters B_0, a_i, b_i, and sewing points R_1 and R_2 of the dipole moment function of the LiH molecule, as well as the atomic constants β_{Li} and β_{H} are summarized in Table 2.

The dipole moment function of the LiH molecule, calculated in this work with the parameters from Table 2, is shown in Fig. 2. For a comparison, Fig. 2 shows also the results of the recent *ab initio* calculations of the dipole moment function,[2–4] as well as the function $\mu(R)$, calculated by Eq. (2) with the experimental parameters $M_0 = \mu_e = 5.82775$ D, $M_1 = \mu_e^{(1)} = 3.238$ D, and $M_2 = \mu_e^{(2)}/2 = 1.00$ D (see Table 1).

Table 2. Parameters of the dipole moment function of the LiH molecule

Parameter	Value	Parameter	Value
a_3, D · Å^{-3}	142.51922	b_2, D · Å^{-2}	–37.02150
a_4, D · Å^{-4}	–475.63918	b_3, D · Å^{-3}	17.30803
a_5, D · Å^{-5}	725.69505	b_4, D · Å^{-4}	–3.83375
a_6, D · Å^{-6}	–639.18248	b_5, D · Å^{-5}	0.31367
a_7, D · Å^{-7}	346.69043	B_0, D · Å^{-6}	423.68627
a_8, D · Å^{-8}	–114.98426	C_7, D · Å^{7}	18148
a_9, D · Å^{-9}	21.49483	R_1, Å	1.70
a_{10}, D · Å^{-10}	–1.74180	R_2, Å	4.05
b_0, D	–12.61342	β_{Li}, a.u.	0.629
b_1, D · Å^{-1}	40.10369	β_{H}, a.u.	1

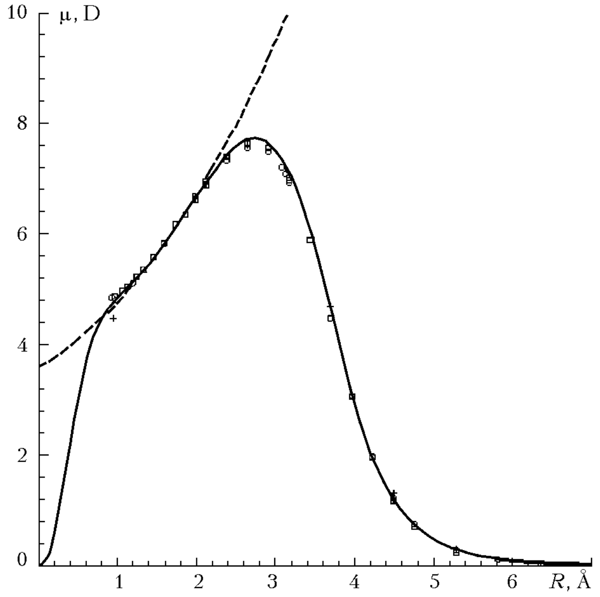

Fig. 2. Dipole moment function of the LiH molecule: this work (solid line), Taylor series (2) with the experimental values of M_i (i = 0, 1, 2) (dashed line), *ab initio* calculation from Ref. 2 (squares), *ab initio* calculation from Ref. 3 (crosses), *ab initio* calculation from Ref. 4 (circles).

The analysis of the functions shown in Fig. 2 shows that the calculated dipole moment function is in a good agreement with the *ab initio* calculations of $\mu(R)$ [Refs. 2–4] in the range $0.9 \le R \le 10$ Å and with the experimental $\mu(R)$ values in the range $0.9 \le R \le 2.4$ Å.

Conclusions

In this paper, we have used a semi-empirical method for construction of the dipole moment function of the LiH molecule. This method has allowed us to better interpret the behavior of this function in the entire range of the internuclear distance. The dipole moment function obtained well agrees with the experimental data, has the correct asymptotic behavior at small and large internuclear distances, and, in our opinion, it is close to the real one. The values of the second and third derivatives of the dipole moment, presented in Table 1, are likely close to the real ones too.

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