

QUANTITATIVE ANALYSIS  
OF VIBRATION-ROTATIONAL SPECTRA  
OF DIATOMIC MOLECULES  
WITH  $(v, J)$ -DEPENDENT  
DYNAMICAL REFERENCE CONFORMATION.  
APPLICATION TO LiH  $X^1\Sigma^+$

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*(Received May 11, 1999)*

An extension of deformationally self-consistent approach to a quantitative analysis of adiabatic and nonadiabatic effects in vibration-rotational spectra of diatomic molecules is presented. We consider vibrational displacements of nuclei in the vicinity of dynamical reference conformation  $R_{v,J}$  that depends not only on the rotational quantum number  $J$  through the action of centrifugal force, but also on the vibrational  $v$  one, through nonadiabatic vibrational effects of high order. The method is applied to LiH  $X^1\Sigma^+$ ; reported wave numbers of transitions are reproduced with  $\hat{\sigma} = 1.090$  and  $F = 5.98 \times 10^{14}$  using 14 independently adjusted parameters and 14 constrained parameters  $t_{i=0-6}^{Li,H}$ , representing nonadiabatic rotational effects. The latter have been evaluated from the rotational  $g$ -factor and electric dipole moment of LiH, both electronically computed.

PACS numbers: 33.15.Mt, 33.20.Vq

## 1. Introduction

Highly resolved infrared and microwave spectra of diatomic molecules are the source of important information about the internal structure and physical properties of the latter including mechanical, extra-mechanical and electromagnetic molecular properties. The mechanical effects are customarily discussed in terms of a Born-Oppenheimer (BO) function of internuclear potential energy expanded as a series

$$V(R) = c_0 \xi^2 \left( 1 + \sum_{i=1} c_i \xi^i \right), \quad \xi = \begin{cases} (R - R_0)/R_0 & \text{(a)} \\ (R - R_0)/R & \text{(b)} \\ 2(R - R_0)/(R + R_0) & \text{(c)} \end{cases} \quad (1)$$

in the vicinity of the BO reference conformation  $R_0$ . For a chosen coordinate  $\xi$  we obtain the common (1a) Dunham [1], (1b) Simons-Parr-Finlan [2] and (1c) Ogilvie [3] expansions, respectively.

Extra-mechanical properties include adiabatic and nonadiabatic effects. The former are attributed to the dependence of internuclear potential energy not only on internuclear distance but also on relative nuclear momenta, whereas the latter appear because electrons fail to follow the nuclei perfectly during their rotational and vibrational motions. Adiabatic effects involve only the electronic ground state  $X^1\Sigma^+$  or  $0^+$  for vibration-rotational spectra, whereas nonadiabatic effects are expressed in terms of matrix elements connecting the electronic ground state and electronically excited states, commonly  $^1\Pi$  for rotational effects [4].

In a quantitative analysis of molecular spectra these extra-mechanical properties are represented by radial functions [5]

$$V'(R) = m_e \sum_{i=1} \sum_{\mu=a,b} u_i^\mu m_\mu^{-1} \xi^i, \quad (2)$$

$$\alpha(R) = m_e \sum_{i=0} \sum_{\mu=a,b} t_i^\mu m_\mu^{-1} \xi^i, \quad (3)$$

$$\beta(R) = m_e \sum_{i=0} \sum_{\mu=a,b} s_i^\mu m_\mu^{-1} \xi^i, \quad (4)$$

describing the adiabatic  $V'(R)$ , nonadiabatic rotational  $\alpha(R)$  and nonadiabatic vibrational  $\beta(R)$  effects. In the above formulae  $m_e$ ,  $m_a$ ,  $m_b$ ,  $m$  are masses of electron, nuclei and reduced mass of the nuclei, respectively.

Electromagnetic properties of a molecule, including its dipole moment, electric polarity, and rotational  $g$ -factor connected with a molecular magnetizability, can be deduced from the parameters  $t_i^{a(b)}$  appearing in (3). They are related [4] to the rotational  $g$ -factor  $g_J$  and electric dipole moment  $\mu$  (for an assumed polarity  $^+AB^-$ ) in the following manner:

$$g_J(R) = m_p \sum_{i=0} \sum_{\mu=a,b} t_i^\mu m_\mu^{-1} \xi^i, \quad (5)$$

$$\mu(R) = (eR/2) \sum_{i=0} (t_i^a - t_i^b) \xi^i. \quad (6)$$

In the above equations  $m_p$  is protonic mass and  $e$  is protonic charge.

A standard procedure for evaluation of radial functions  $V(R)$ ,  $V'(R)$ ,  $\alpha(R)$ ,  $\beta(R)$  from pure rotational and vibration-rotational spectra of diatomic species in an electronic ground state  $X^1\Sigma^+$  or  $0^+$  is based on a theoretical model developed by Herman and Asgharian [6] containing subsequent refinements by Bunker [7], Watson [8], Herman and Ogilvie [9], and by Ogilvie [10-12]. This approach applies an analytic formalism originated by Dunham [1] but with a treatment greatly extended to include adiabatic and nonadiabatic effects.

Another method is based on the deformable-body model (DBM) [13] and a deformationally self-consistent (DS-c) procedure (DS-cP) [14] of the treatment of spectral data. This approach was tested first on single isotopomers of several diatomic molecules [13, 14], and then applied in the quantitative analysis of adiabatic and nonadiabatic rotational effects in GaH [15], LiH [16], and GeS [17] providing a satisfactory reproduction of the transitions detected by making use of fewer fitting parameters than in the standard approach [18–20]. Because the available spectral data were insufficient to allow a separate evaluation of  $\beta(R)$  representing nonadiabatic vibrational effects, we used in calculations the simplified DS-cP with all parameters  $s_i^{a(b)}$  constrained to zero.

The main aim of this paper is an extension of our method to include nonadiabatic vibrational effects (NVE) in the DBM and DS-c scheme. In comparison to our previous model we consider vibrational displacements of nuclei in the vicinity of dynamical reference conformation  $R_{vJ}$  that depends not only on the rotational quantum number  $J$ , through the action of centrifugal force, but also on the vibrational  $v$  one, through nonadiabatic vibrational effects of high order. For a test calculation we apply the generalized DS-cP to the simultaneous analysis of pure rotational and vibration-rotational spectra of  ${}^7\text{Li}^1\text{H}$ ,  ${}^6\text{Li}^1\text{H}$ ,  ${}^7\text{Li}^2\text{H}$ , and  ${}^6\text{Li}^2\text{H}$  in a scheme with constrained  $t_i^{a(b)}$  parameters. The latter were determined [4, 12] from the rotational  $g$ -factor and dipole moment of LiH, both from quantum-chemical calculations. Such an approach requires an application of high order parameters  $s_i^{a(b)}$  to achieve the satisfactory reproduction of the spectra; hence it is useful for the test purpose. In the final part of the paper we introduce a parameter characterizing molecular susceptibility to rotational and vibrational deformation; it is a new property of molecules, evaluated from rotation-vibrational spectra, being an objective criterion of molecular rigidity.

## 2. Method

The standard procedure for the reduction of spectral data, comprising wave numbers of pure rotational and vibration-rotational transitions, to parameters of radial functions (1)–(4) is based on the wave equation derived by Herman and Asgharian [6]

$$\left\{ -\frac{\hbar^2}{2m} \frac{d}{dR} [1 + \beta(R)] \frac{d}{dR} + U_J(R) - E_{vJ} \right\} \psi_{vJ}(R) = 0, \quad (7)$$

$$U_J(R) = \frac{\hbar^2 J(J+1)[1 + \alpha(R)]}{2mR^2} + V(R) + V'(R) \quad (8)$$

or in an equivalent form [21]

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + [U_J(R) + \gamma(R) - E_{vJ}] / [1 + \beta(R)] \right\} \psi_{vJ}(R) = 0, \quad (9)$$

in which

$$\gamma(R) = \frac{\hbar^2}{2m} \left[ \frac{1}{2} \frac{d^2\beta(R)}{dR^2} - \left( \frac{d\beta(R)}{dR} \right)^2 \frac{1}{4[1 + \beta(R)]} \right], \quad (10)$$

$$\Psi_{vJ}(R) = \psi_{vJ}(R)[1 + \beta(R)]^{1/2}. \quad (11)$$

The nonadiabatic functions  $\alpha(R)$ ,  $\beta(R)$ , appearing in (7), have the same absolute order  $(m_e/m)^2$  according to the nature of electronic matrix elements that they represent [12, 21]. However, relative to their addends of unity they appear in (9) as functions of intrinsic order  $m_e/m$ ; similarly adiabatic term  $V'(R)$  is of the same order  $m_e/m$  relative to BO potential  $V(R)$  [12]. Consequently, the wave equation (7) can be significantly simplified by applying the linear approximation [12]

$$[1 + \beta(R)]^{-1} \approx 1 - \beta(R) \quad (12)$$

and ignoring all terms containing a ratio of electronic to nuclear mass to powers greater than  $m_e/m$  [12]. As a result we obtain the Schrödinger equation [12]

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + U_{vJ}(R) - E_{vJ} \right] \Psi_{vJ}(R) = 0, \quad (13)$$

$$U_{vJ}(R) = \frac{\hbar^2 J(J+1)[1 + \alpha(R) - \beta(R)]}{2mR^2} + V(R)[1 - \beta(R)] + V'(R) + E_{vJ}\beta(R) \quad (14)$$

amenable to semi-classical Wentzel-Kramers-Brillouin (WKB) treatment, provided that  $E_{vJ}$  appearing in (14) is treated as a known power series expansion in  $J$  and  $v$  [6]. To this effect another approximation [6]

$$E_{vJ} \approx E_{vJ}^{\text{BO}} \quad (15)$$

is used, in which  $E_{vJ}^{\text{BO}}$  denotes the BO term values obtained by solving Eq. (13) for  $s^{a(b)} = t^{a(b)} = u^{a(b)} = 0$ .

To obtain eigenvalues of the wave equation (13) one expands [5, 12] the effective potential (14) into a series of Dunham's coordinate  $x = (R - R_0)/R_0$  and then one applies Dunham's semi-classical approach [1] or hypervirial theorem [10], variational [22], or perturbational [23] method. For the first two cases, the eigenvalues take the form [5, 12]

$$E_{vJ} = \sum_{k,l=0} (Y_{kl} + Z_{kl}^{r,a(b)} + Z_{kl}^{v,a(b)})(v + 1/2)^k [J(J+1)]^l, \quad (16)$$

in which  $Y_{kl}$  are Dunham's term coefficients depending on  $R_0$  and  $c_i$ , whereas  $Z_{kl}^{r,a(b)}$  and  $Z_{kl}^{v,a(b)}$  represent adiabatic and rotational (vibrational) nonadiabatic terms depending on  $u_i^{a,b}$ ,  $t_i^{a,b}$  and  $s_i^{a,b}$ ;  $J$  and  $v$  are rotational and vibrational quantum numbers, respectively.

As was pointed out, a standard procedure to derive eigenvalues (16) is based on an expansion of  $U_{vJ}(R)$  into a series of Dunham's variable  $x = (R - R_0)/R_0$ . This approach seems to be justified [15] only for purely vibrational systems described by the BO potential (1). In a more general case of molecules endowed with the effective potential (14), vibrational displacements of nuclei take place in a vicinity of a modified equilibrium conformation  $R_{vJ}$  defined according to the criterion for a minimum

$$\left[ \frac{dU_{vJ}(R)}{dR} \right]_{R=R_{vJ}} = 0. \quad (17)$$

An alteration  $R_0 \rightarrow R_{vJ}$  is a result of the centrifugal deformation [14-17] and NVE of high order ( $s_i^{a(b)}$ ) responsible for the appearance of the term  $E_{vJ}\beta(R)$  in the effective potential (14) and additional  $v$ -dependence of  $R_{vJ}$ .

Starting from this basic idea we express all terms in the wave equation (13) by a  $(v, J)$ -dependent variable

$$\eta = \frac{R - R_{vJ}}{R_{vJ}}, \quad (18)$$

applying the linear transformation

$$x = x_{vJ} + \eta(1 + x_{vJ}), \quad x_{vJ} = \frac{R_{vJ} - R_0}{R_0}, \quad (19)$$

in which

$$x = (R - R_0)/R_0 \quad (20)$$

is Dunham's coordinate. In this way we obtain

$$\left[ -B_{vJ} \frac{d^2}{d\eta^2} + U_{vJ}(\eta) - E_{vJ} \right] \Psi_{vJ}(\eta) = 0, \quad (21)$$

in which

$$B_{vJ} = \hbar^2 / [2m(R_{vJ})^2] \quad (22)$$

denotes an effective rotational constant, whereas

$$U_{vJ}(\eta) = \frac{B_{vJ}J(J+1)[1 + \alpha(\eta) - \beta(\eta)]}{(1 + \eta)^2} + V(\eta)[1 - \beta(\eta)] + V'(\eta) + E_{vJ}\beta(\eta) \quad (23)$$

is an effective potential.

Expanding (23) into a series of variable  $\eta$

$$U_{vJ}(\eta) = \sum_{n=0} b_n^{vJ} \eta^n, \quad (24)$$

$$b_n^{vJ} = (n!)^{-1} [d^n U_{vJ}(\eta) / d\eta^n]_{\eta=0}, \quad (25)$$

we arrive at the Schrödinger equation

$$\left( -B_{vJ} \frac{d^2}{d\eta^2} + \sum_{n=0} b_n^{vJ} \eta^n - E_{vJ} \right) \psi_{vJ}(\eta) = 0, \quad (26)$$

and quantum-mechanical force (in Heisenberg's representation)

$$\hat{p} = (i\hbar)^{-1} [\hat{p}, \hat{H}] = -\frac{dU_{vJ}(\eta)}{d\eta}, \quad (27)$$

in which  $\hat{H}$  is a Hamiltonian operator appearing in (21).

The dynamical equilibrium state between deforming and restoring potential forces is achieved when

$$\hat{p} = 0 \implies \left[ \frac{dU_{vJ}(\eta)}{d\eta} \right]_{\eta=0} = b_1^{vJ} = 0, \quad (28)$$

we consequently exclude a linear term  $b_1^{vJ} \eta$  from (24) generating the effective Schrödinger equation

$$\left[ -B_{vJ} \frac{d^2}{d\eta^2} + a_0^{vJ} \eta^2 \left( 1 + \sum_{s=1} a_s^{vJ} \eta^s \right) - (E_{vJ} - b_0^{vJ}) \right] \psi_{vJ}(\eta) = 0, \quad (29)$$

in which  $a_0^{vJ} = b_2^{vJ}$ ,  $a_{s>0}^{vJ} = b_{s+2}^{vJ}/a_0^{vJ}$ .

Equation (29) is amenable to straightforward solution in the WKB scheme [1] providing the term values

$$E_{vJ} = b_0^{vJ} + \sum_{k=0} Y_{k0}(v+1/2)^k, \quad (30)$$

in which

$$b_0^{vJ} = B_{vJ} J(J+1)[1 + \alpha(0) - \beta(0)] \\ + V(R_{vJ})[1 - \beta(0)] + V'(0) + E_{vJ} \beta(0) \quad (31)$$

and  $Y_{k0}$  are purely Dunham's vibrational coefficients  $Y_{k0}$  [1], in which substitutions  $\{R_0, a_n\} \rightarrow \{R_{vJ}, a_n^{vJ}\}$  are made.

### 3. Generalized DS-c procedure

The obtained energies (30) depend not only on an unknown parameter  $R_{vJ}$ , defined according to a general equilibrium condition (17)

$$b_1^{vJ}(E_{vJ}, R_{vJ}, q_i) = 0, \quad (32)$$

in which

$$q_i = (R_0, c_n, s_i^{a(b)}, t_i^{a(b)}, u_i^{a(b)}), \quad (33)$$

but also on the energy levels  $E_{vJ}$  hidden in the coefficients  $b_n^{vJ}$ . To determine parameters  $q_i$  from spectral data we must consequently work either in the DS-c scheme with one circulating parameter  $x_{vJ} = (R - R_{vJ})/R_{vJ}$  assuming  $E_{vJ} \approx E_{vJ}^{\text{BO}}$ , or in the generalized DS-c approach with two circulating parameters  $x_{vJ}$  and  $E_{vJ}$ . The second case is interesting as then we eliminate the approximation (15) employed in the standard scheme. Here we work with a doubly iterative scheme involving two circulating parameters.

For the initial values of  $E_{vJ} = E_{vJ}^{\text{BO}}$  and  $q_i$ , the roots  $R_{vJ}$  of Eq. (28) are calculated using Newton-Raphson algorithm. After substitution of  $R_{vJ}$  and  $E_{vJ} = E_{vJ}^{\text{BO}}$  into eigenvalues (30) the parameters  $q_i$  are fitted to experimental data using a weighted nonlinear least-squares routine with weights taken as the inverse squares of uncertainties of experimental data. The parameters  $q_i$  and new values of  $E_{vJ}$  evaluated in the previous step are again introduced to (32) allowing evaluation of a more accurate value of  $R_{vJ}$  employed to calculate the new values of  $q_i$  and  $E_{vJ}$ . This iterative procedure is continued to obtain the best fit according to the following criteria: the minimum number of fitted parameters  $N$  consistent with the minimum value of normalized standard deviation  $\hat{\sigma} \approx 1$ , the maximum value of  $F$ -statistic, and the optimal values of estimated standard error  $\sigma_i$  of each fitted parameter  $i$  and of correlation coefficient  $cc(i, j)$  between parameters  $i$  and  $j$ .

## 4. Application

The proposed method is tested on spectral data of  ${}^7\text{Li}^1\text{H}$ ,  ${}^6\text{Li}^1\text{H}$ ,  ${}^7\text{Li}^2\text{H}$ , and  ${}^6\text{Li}^2\text{H}$ , investigated in Refs. [4, 22]. These data comprise 543 unduplicated rotational and vibration-rotational transitions measured with an individual precision from  $1.67 \times 10^{-6} \text{ cm}^{-1}$  to  $1.0 \times 10^{-3} \text{ cm}^{-1}$  [24–28].

TABLE I

Radial parameters<sup>a</sup> of  $\text{LiH } X^1\Sigma^+$  generated by Radiatom programme and DS-cP.

	Radiatom	DS-cP
$c_0$ [ $\text{cm}^{-1}$ ]	65724.857(72)	65723.17(10)
$c_1$	-0.897208(12)	-0.897091(15)
$c_2$	0.347847(76)	0.348249(30)
$c_3$	-0.086373(42)	-0.08863(38)
$c_4$	-0.04529(18)	-0.04611(72)
$c_5$	-0.0307(52)	-
$c_6$	0.0921(96)	-
$u_1^{\text{Li}}/10^4$ [ $\text{cm}^{-1}$ ]	-5.740(44)	-5.704(45)
$u_1^{\text{H}}/10^4$ [ $\text{cm}^{-1}$ ]	-5.2787(31)	-5.2706(44)
$u_2^{\text{H}}/10^4$ [ $\text{cm}^{-1}$ ]	7.245(70)	6.452(55)
$u_3^{\text{H}}/10^4$ [ $\text{cm}^{-1}$ ]	-7.53(14)	-7.02(19)
$u_4^{\text{H}}/10^4$ [ $\text{cm}^{-1}$ ]	-	9.55(58)
$s_0^{\text{Li}}$	-0.194(11)	2.064(14)
$s_0^{\text{H}}$	-0.567(10)	-0.4359(86)
$s_2^{\text{H}}$	-0.591(112)	-2.99(17)
$R_0$ [ $\text{\AA}$ ]	1.594912(14)	1.59491217(51)
$\hat{\sigma}$	1.095	1.090
$F$	$5.0 \times 10^{14}$	$5.98 \times 10^{14}$

<sup>a</sup>All parameters  $t_{i=0-6}^{\text{Li}}$  and  $t_{i=0-6}^{\text{H}}$  are constrained to the values specified in Ref. [12].

Table I presents the values of radial parameters obtained in a standard approach employing Radiatom programme [5, 6, 12], and in a generalized DS-c scheme. The uncertainty in parentheses is a one-estimated standard error in units of the last quoted digit of the fitted values. In the calculation 14 parameters  $t_{i=0-6}^{a(b)}$  were constrained to the values specified in Ref. [12]; all other parameters were constrained to zero. The parameters  $t_{i=0-6}^{a(b)}$  were calculated [6, 12] from the relationships [6]

$$\sum_{i=0} t_i^{\text{Li}} z^i = m[g_J(R)/m_p + 2\mu(R)/eRm_{\text{H}}], \quad (34)$$

$$\sum_{i=0} t_i^H z^i = m[g_J(R)/m_p - 2\mu(R)/eRm_{Li}], \quad (35)$$

$$z = 2(R - R_0)/(R + R_0), \quad (36)$$

including the rotational  $g$ -factor  $g_J(R)$  and the electric dipolar moment  $\mu(R)$  of LiH, both electronically computed.

Working in the DS-c scheme we used Dunham's vibrational coefficients [1]

$$Y_{k0} = \sum_{h=0}^3 Y_{k0}^{2h}, \quad (37)$$

up to the sixth order for  $0 \leq k \leq 4$ , including  $a_n$ ,  $0 \leq n \leq 6$  potential parameters. The expansion coefficients  $b_n^{vJ}$  of effective potential energy (24) contain the derivatives up to eighth order calculated using the Maple processor.

The proposed iterative DS-cP with 2 circulating parameters requires in the case of LiH 15 iterations to produce parameters in a final set such that the values alter less than their standard errors, and affect insignificantly the precision of the calculations. The initial values of the fitted parameters were taken from Ogilvie's calculation [12].

In Table II, the parameters  $x_{vJ} = (R_{vJ} - R_0)/R_0$  for LiH in four isotopic variants are reported; they are evaluated with an accuracy  $\epsilon = 10^{-15}$  to be achieved in 30 iterations using the Newton-Raphson procedure. The quantity  $x_{00}$  in Table II denotes an adiabatic-nonadiabatic reference conformation defined according to the criterion of minimum potential energy

$$U_{v0}(\eta) = V(\eta)[1 - \beta(\eta)] + V'(\eta) + E_{v0}\beta(\eta). \quad (38)$$

## 5. Results and discussion

The application of the generalized DS-cP with two circulating parameters enables a reduction of wave numbers of 543 rotational and vibration-rotational transitions of LiH to 14 independently adjustable radial parameters reproducing the reported wave numbers within 1.09 times (on average) the uncertainties of the measurements. The value of the  $F$ -statistic was  $5.98 \times 10^{14}$ ; deviations of only 8 data exceed three specified uncertainties, none greater than 4.57, and 397 lines were reproduced within 1.00 or less stated uncertainties of measurements. Of 91 independent values of correlation coefficients from the matrix of variance and covariance, only two magnitudes exceed 0.96;  $cc(u_2^H, s_0^H) = 0.967$  and  $cc(c_3, c_4) = 0.981$ .

Fitting data with parameters quoted in Table I, enriched with  $c_5$  and  $c_6$ , we evaluated  $c_5 = -0.0014(53)$  and  $c_6 = 0.017(11)$  with  $\hat{\delta} = 1.071$  and  $F = 5.25 \times 10^{14}$ . Hence, by the virtue of the criterion of the maximal  $F$ -statistic we eliminated  $c_5$  and  $c_6$  from the final parameter set; their omission only slightly deteriorates the accuracy of spectral reproduction. These results differ from those of Ogilvie [12], who evaluated  $c_5 = -0.0307(52)$  and  $c_6 = 0.0921(96)$ ; they were indispensable to fit the input data.

TABLE II  
 Mass-dependent deformational parameters  $x_{vJ} = (R_{vJ} - R_0)/R_0$  for LiH.

$J$	$v$	${}^7\text{Li}{}^1\text{H}$	${}^7\text{Li}{}^2\text{H}$	${}^6\text{Li}{}^1\text{H}$	${}^6\text{Li}{}^2\text{H}$
0	0	$2.52156788 \times 10^{-4}$	$1.43151361 \times 10^{-4}$	$2.57811960 \times 10^{-4}$	$1.48803420 \times 10^{-4}$
0	1	$2.52165313 \times 10^{-4}$	$1.43153194 \times 10^{-4}$	$2.57820764 \times 10^{-4}$	$1.48805359 \times 10^{-4}$
0	2	$2.52173558 \times 10^{-4}$	$1.43154981 \times 10^{-4}$		$1.48807250 \times 10^{-4}$
1	0	$4.80809278 \times 10^{-4}$	$2.71969051 \times 10^{-4}$	$4.91243868 \times 10^{-4}$	$2.82402282 \times 10^{-4}$
1	1	$4.80825533 \times 10^{-4}$	$2.71972533 \times 10^{-4}$	$4.91260644 \times 10^{-4}$	$2.82405962 \times 10^{-4}$
1	2	$4.80841252 \times 10^{-4}$	$2.71975929 \times 10^{-4}$	$4.91276861 \times 10^{-4}$	$2.82409550 \times 10^{-4}$
1	3		$2.71979240 \times 10^{-4}$		
2	0	$9.38066837 \times 10^{-4}$	$5.29589240 \times 10^{-4}$	$9.58058284 \times 10^{-4}$	$5.49583674 \times 10^{-4}$
2	1	$9.38098548 \times 10^{-4}$	$5.29596021 \times 10^{-4}$	$9.58090998 \times 10^{-4}$	$5.49590837 \times 10^{-4}$
2	2	$9.38129215 \times 10^{-4}$	$5.29602633 \times 10^{-4}$	$9.58122622 \times 10^{-4}$	$5.49597819 \times 10^{-4}$
2	3		$5.29609081 \times 10^{-4}$		
3	0	$1.62383536 \times 10^{-3}$	$9.15981682 \times 10^{-4}$	$1.65815719 \times 10^{-3}$	$9.50315082 \times 10^{-4}$
3	1	$1.62389025 \times 10^{-3}$	$9.15993409 \times 10^{-4}$	$1.65821380 \times 10^{-3}$	$9.50327466 \times 10^{-4}$
3	2	$1.62394333 \times 10^{-3}$	$9.16004845 \times 10^{-4}$	$1.65826852 \times 10^{-3}$	$9.50339538 \times 10^{-4}$
3	3		$9.16015996 \times 10^{-4}$	$1.65832140 \times 10^{-3}$	
4	0	$2.53797556 \times 10^{-3}$	$1.43110133 \times 10^{-3}$	$2.59139552 \times 10^{-3}$	$1.48454810 \times 10^{-3}$
4	1	$2.53806133 \times 10^{-3}$	$1.43111965 \times 10^{-3}$	$2.59148398 \times 10^{-3}$	$1.48456744 \times 10^{-3}$
4	2	$2.53814427 \times 10^{-3}$	$1.43113752 \times 10^{-3}$	$2.59156949 \times 10^{-3}$	$1.48458630 \times 10^{-3}$
4	3	$2.53822444 \times 10^{-3}$	$1.43115494 \times 10^{-3}$	$2.59165212 \times 10^{-3}$	$1.48460468 \times 10^{-3}$
5	0	$3.68030510 \times 10^{-3}$	$2.07488877 \times 10^{-3}$	$3.75758350 \times 10^{-3}$	$2.15221888 \times 10^{-3}$
5	1	$3.68042945 \times 10^{-3}$	$2.07491532 \times 10^{-3}$	$3.75771174 \times 10^{-3}$	$2.15224692 \times 10^{-3}$
5	2	$3.68054970 \times 10^{-3}$	$2.07494122 \times 10^{-3}$	$3.75783571 \times 10^{-3}$	$2.15227426 \times 10^{-3}$
5	3	$3.68066593 \times 10^{-3}$	$2.07496648 \times 10^{-3}$	$3.75795549 \times 10^{-3}$	$2.15230090 \times 10^{-3}$
5	4		$2.07499109 \times 10^{-3}$		
10	0	$1.28058202 \times 10^{-2}$	$7.22083139 \times 10^{-3}$	$1.30734415 \times 10^{-2}$	$7.48890881 \times 10^{-3}$
10	1	$1.28062522 \times 10^{-2}$	$7.22092373 \times 10^{-3}$	$1.30738871 \times 10^{-2}$	$7.48900630 \times 10^{-3}$
10	2	$1.28066700 \times 10^{-2}$	$7.22101378 \times 10^{-3}$	$1.30743176 \times 10^{-2}$	$7.48910133 \times 10^{-3}$
10	3	$1.28070736 \times 10^{-2}$	$7.22110158 \times 10^{-3}$		$7.48919393 \times 10^{-3}$
15	0	$2.75908287 \times 10^{-2}$	$1.55675391 \times 10^{-2}$	$2.81661303 \times 10^{-2}$	$1.61444913 \times 10^{-2}$
15	1	$2.75917575 \times 10^{-2}$	$1.55677379 \times 10^{-2}$	$2.81670879 \times 10^{-2}$	$1.61447012 \times 10^{-2}$
15	2	$2.75926552 \times 10^{-2}$	$1.55679318 \times 10^{-2}$	$2.81680132 \times 10^{-2}$	$1.61449058 \times 10^{-2}$
15	3		$1.55681207 \times 10^{-2}$		
20	0	$4.79922913 \times 10^{-2}$	$2.70966813 \times 10^{-2}$	$4.89914963 \times 10^{-2}$	$2.80994998 \times 10^{-2}$
20	1	$4.79939026 \times 10^{-2}$	$2.70970268 \times 10^{-2}$		$2.80998645 \times 10^{-2}$
20	2	$4.79954591 \times 10^{-2}$	$2.70973637 \times 10^{-2}$		$2.81002199 \times 10^{-2}$
30	0		$5.96329692 \times 10^{-2}$		
30	1		$5.96337266 \times 10^{-2}$		

Absent from the set of the fitted parameters is  $s_1^{\text{H}}$  but  $s_2^{\text{H}} = -2.99(17)$  is significantly evaluated, in comparison with  $s_2^{\text{H}} = -0.591(113)$  in the conventional scheme [12]. In the preliminary fits of data in which  $s_1^{\text{H}}$  and  $s_1^{\text{Li}}$  were allowed to vary, we discovered that their magnitudes were relatively small and associated

with relatively large errors, moreover their presence in the fit led to the divergent DS-cP due to a strong correlation between  $s_1^H$ ,  $s_1^{Li}$  and other parameters. We thus decided to constrain their values to zero. A similar condition arose in the standard approach [12].

According to the method employing the Radiatom programme, a fit of the same data required 17 free fitted parameters and 11 parameters  $t_{i=0-6}^{Li}$ ,  $t_{i=0-3}^H$  [4] constrained; the normalized standard deviation was 1.095 whereas the  $F$  value  $5.0 \times 10^{14}$ . Fitting the same data with 14 parameters  $t_{i=0-6}^{Li}$ ,  $t_{i=0-6}^H$  constrained, Ogilvie [12] evaluated 15 adjustable parameters, at the same statistical characteristic of the fits (J.F. Ogilvie — private communication). Thus, we conclude that the reduction in the DS-c scheme of 543 spectral data of LiH to 14 radial parameters in Table I is more efficient than the one obtained previously [12].

The inspection of Table II reveals that a dynamical reference conformation  $R_{vJ}$  of LiH increases not only with  $J$  because of centrifugal force but also slightly with  $v$  because of NVE of order greater than zero (for  $s_{i>0}^{\alpha(b)}$ ). This effect was not previously reported in the theoretical spectroscopy.

TABLE III

Mass-dependent deformational parameter  $x_{01} = (R_{01} - R_0)/R_0$  for various diatomic molecules.

	Ref.	$x_{01}$
LiH		$2.71 \times 10^{-4}$ – $4.91 \times 10^{-4}$
GaH	[15]	$5.97 \times 10^{-5}$ – $1.17 \times 10^{-4}$
ArH <sup>+</sup>	[31]	$6.10 \times 10^{-5}$ – $1.16 \times 10^{-4}$
NaCl	[29]	$2.80 \times 10^{-6}$ – $2.86 \times 10^{-6}$
N <sub>2</sub>	[30]	$5.36 \times 10^{-6}$ – $5.74 \times 10^{-6}$
GeS	[17]	$8.24 \times 10^{-7}$ – $8.58 \times 10^{-7}$
BrCl	[31]	$9.00 \times 10^{-7}$ – $9.42 \times 10^{-7}$

A parameter  $x_{vJ} = (R_{vJ} - R_0)/R_0$  is a source of important information on molecular susceptibility to rotational ( $v = 0$ ,  $J = 1$ ) deformation; this piece of information is unavailable in a standard approach. The value of  $x_{01}$  is known for LiH (see Table II), GaH [15], GeS [17], NaCl [29], N<sub>2</sub> [30], ArH<sup>+</sup> and BrCl [31]; they are reported in Table III. Its inspection reveals that GaH, ArH<sup>+</sup> and LiH may be classified as *soft*, N<sub>2</sub> and NaCl as *semi-rigid*, whereas BrCl and GeS as *rigid* molecules.

#### Acknowledgment

I am indebted to Prof. J.F. Ogilvie for providing data of LiH and Prof. J. Konarski for helpful discussions.

## References

- [1] J.L. Dunham, *Phys. Rev.* **41**, 713, 721 (1932).
- [2] G. Simons, R.G. Parr, J.M. Finlan, *J. Chem. Phys.* **59**, 3229 (1973).
- [3] J.F. Ogilvie, *Proc. R. Soc. Lond. A* **378**, 287 (1981).
- [4] J.F. Ogilvie, J. Oddershede, S.P.A. Sauer, *Chem. Phys. Lett.* **228**, 183 (1994).
- [5] J.F. Ogilvie, *J. Phys. B* **27**, 47 (1994).
- [6] R.M. Herman, A. Asgharian, *J. Mol. Spectrosc.* **19**, 305 (1966).
- [7] P.R. Bunker, *J. Mol. Spectrosc.* **35**, 306 (1970).
- [8] J.K.G. Watson, *J. Mol. Spectrosc.* **80**, 411 (1980).
- [9] R.M. Herman, J.F. Ogilvie, *Adv. Chem. Phys.* **103**, 287 (1998).
- [10] F.M. Fernández, J.F. Ogilvie, *Chin. J. Phys.* **30**, 177 (1992).
- [11] F.M. Fernández, J.F. Ogilvie, *Phys. Rev. A* **42**, 4001 (1990).
- [12] J.F. Ogilvie, *The Vibrational and Rotational Spectrometry of Diatomic Molecules*, Academic Press, London 1998.
- [13] M. Molski, *J. Mol. Spectrosc.* **168**, 404 (1994).
- [14] M. Molski, *Phys. Rev. A* **50**, 4380 (1994).
- [15] M. Molski, *J. Mol. Spectrosc.* **181**, 1 (1997).
- [16] M. Molski, *J. Mol. Spectrosc.* **185**, 256 (1997).
- [17] M. Molski, *J. Mol. Spectrosc.* **193**, 244 (1999).
- [18] J.F. Ogilvie, S.C. Liao, *Chem. Phys. Lett.* **226**, 281 (1994).
- [19] J.F. Ogilvie, *J. Mol. Spectrosc.* **180**, 193 (1996).
- [20] J.F. Ogilvie, *Mol. Phys.* **88**, 1055 (1996).
- [21] P.R. Bunker, R.E. Moss, *Mol. Phys.* **33**, 417 (1977).
- [22] K. Nakagawa, H. Uehara, *Chem. Phys. Lett.* **168**, 96 (1990).
- [23] A.V. Burenin, M.Yu. Ryabikin, *J. Mol. Spectrosc.* **136**, 140 (1989).
- [24] G.M. Plummer, E. Herbst, F.C. Lucia, *J. Chem. Phys.* **81**, 4893 (1984).
- [25] A.G. Maki, W.B. Olson, G. Thompson, *J. Mol. Spectrosc.* **144**, 257 (1990).
- [26] P. de Natale, M. Bellini, M. Inguscio, G. Buffa, O. Tarrini, *J. Mol. Spectrosc.* **163**, 507 (1994).
- [27] M. Bellini, P. de Natale, M. Inguscio, G. Buffa, O. Tarrini, *J. Mol. Spectrosc.* **424**, 507 (1994).
- [28] C. Yamada, E. Hirota, *J. Chem. Phys.* **88**, 6702 (1988).
- [29] J.F. Ogilvie, M. Molski, *Spectrochim. Acta A*, in press.
- [30] M. Molski, *J. Raman. Spectrosc.*, in press.
- [31] M. Molski, in preparation.