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Sensitivity to proton-to-electron mass ratio variation from pairs of isotopic lithium hydride rotational and rovibrational transitions

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Abstract:

Calculations of the sensitivities of rotational and rovibrational transitions of isotopic lithium hydride in the electronic ground state to a variation of the proton-to-electron mass ratio constant are presented. A highly enhanced sensitivity coefficient is observed for the splitting of near resonant transitions arising from a cancellation between rotational intervals and frequency shifts associated respectively to the isotope effect, to the anharmonicity and to the rotation-vibration interaction. It ranges from 73 748.47(1) to $-21\,672(137)$ for the transitions with low to intermediate rotational quantum numbers in the lowest vibrational energy levels. The splittings of rotational transitions of ${}^7\text{LiD}$ in the vibrational level $v = 0$ and ${}^6\text{LiD}$ in the vibrational level $v = 2$ have a sensitivity coefficient of ~ -3 for J up to 29 and that of ${}^6\text{LiH}$ R(0) and ${}^7\text{LiH}$ R(1) rovibrational transitions in the $v = 0 \rightarrow 1$ band has a sensitivity coefficient of -585. The approach allowed comparison of frequency intervals between rotational lines with ammonia inversion lines detected in the microwave spectra of B0218+357 quasar to put constraints to a variation of the proton-to-electron mass ratio.

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1. Introduction

Modern theories predict variation of fundamental constants over cosmological timescales [1]. Atomic and molecular transition frequencies depend on the fine structure constant α and proton-to-electron mass ratio constant $\mu = m_p/m_e$. Atomic transitions are convenient probes for α variation [2]. The fractional variation of μ is expected to be sensibly higher than that of α [3]. Molecular transitions may probe directly variation of μ without admitting the Schmidt model for the nuclear magnetic moment. A variation $\Delta\mu/\mu$ leads to a change of the molecular frequency $\Delta f/f$ determined by the sensitivity coefficient K_μ : $\Delta f/f = K_\mu \Delta\mu/\mu$. The strategy is to measure molecular frequencies with high sensitivity coefficient and signal to noise ratio. An approach was to compare the frequencies of molecular lines recorded in laboratory to that of the corresponding lines detected in astrophysical objects at high redshift. Detection of H_2 electronic-rotation-vibration lines [4], NH_3 rotation-inversion lines [5] and CH_3OH rotation-torsion lines [6] has been addressed and the latter tighten the constraints on the temporal variation of μ at 10^{-17} yr^{-1} level. Another approach was to do absolute measurements of molecular frequencies in laboratory with accurate control of the systematic frequency shifts. Several schemes have been proposed: ammonia fountain [7], molecular hydrogen ions in radiofrequency traps [8], vibrational transitions of trapped molecules [9], two-photon rovibrational transition on a SF_6 molecular beam [10] and the latter put constraints on the temporal variation of μ at $5.6 \times 10^{-14} \text{ yr}^{-1}$ level.

It was noticed that the splitting between two near resonant energy levels with different dependences on α , μ displays an enhanced sensitivity to a variation of the constants. Degenerate molecular levels have been addressed directly by coupling them with a transition. Measurement of this transition provided a sensitive way to test the stability of the fundamental constants. This approach has been demonstrated by the cancellation between rotational energy levels and hyperfine energy levels [11], fine energy levels [12], inversion energy levels [5], hindered internal rotation energy levels [13], respectively between vibrational energy levels and fine energy levels in the ground electronic state [14] and vibrational energy levels in different electronic states [15-17]. A review of these approaches is presented in [18]. This article addresses conjointly LiH rotational and rovibrational transitions in the $X^1\Sigma$ electronic state to demonstrate significant enhancement of the sensitivity coefficient of the frequency splitting between two near resonant transitions. These transitions arise frequently in the molecular spectra from the cancellation between rotational intervals and frequency shifts associated to the isotope effect, to the anharmonicity or to the rotation-

vibration interaction. Measurements of frequency splittings may lead to an enhancement of the sensitivity to a variation of μ constrained by the frequency splittings and the uncertainties associated to the finite linewidth of the lines.

Lithium hydride, the simplest neutral heteropolar diatomic molecule, was the subject of accurate theoretical and experimental investigations [19]. Common isotopic species ${}^6\text{LiH}$, ${}^7\text{LiH}$, ${}^6\text{LiD}$, ${}^7\text{LiD}$ lead to different sets of molecular parameters that depend on μ . This approach allows an analysis beyond Born-Oppenheimer approximation for the sensitivity of molecular spectra to a variation of μ . Lithium hydride is a molecule with high interest for astrophysics [20]. An attempt to detect its rovibrational spectrum has been performed by searching the emission from primordial clouds in forming regions at high redshift $z \sim 200$ [21]. $J = 0 \rightarrow 1$ ${}^7\text{LiH}$ rotational transition of the vibrational ground state has been detected in the microwave spectra of B0218+357 quasar at a redshift of $z \sim 0.68$ [22]. Lithium hydride is also relevant in cold molecules research [23]. The large dipole moment and low mass allowed Stark deceleration of a lithium hydride molecular beam [24]. The main features of isotopic lithium hydride rotational and rovibrational spectrum have been previously described [25]. Theory was refined by including corrections of the Born-Oppenheimer approximation [26]. Rotational spectrum recorded for all isotopomers by microwave spectroscopy [27-29] allowed to define rotational constants and Born-Oppenheimer correction terms. Infrared measurements by high resolution Fourier transform spectroscopy [30] and high resolution infrared diode laser [31] yield precise constants for the lowest vibrational levels.

2. Energy levels, transitions and sensitivities

The expression of the rotation-vibration energy levels is fitted in a semiempirical approach with the form of Dunham expansion [32]:

$$E(v, J) = \sum_{k,l} Y_{kl} (v + 1/2)^k [J(J+1)]^l \quad (1)$$

with J is the rotational angular momentum quantum number and v the vibrational quantum number. The Dunham parameters are expressed as:

$$Y_{kl} = U_{kl} \mu_r^{-(k/2+l)} \left[I + \Delta_{H,kl} m_e/m_H + \Delta_{Li,kl} m_e/m_{Li} + O^2(m_e/m_{H,Li}) \right] \quad (2)$$

In these expressions U_{kl} , $\Delta_{H,kl}$, $\Delta_{Li,kl}$ are isotopically invariant parameters and μ_r is the reduced mass of the diatomic molecule $\mu_r = m_H m_{Li} / (m_H + m_{Li})$ with m_H and m_{Li} are the atomic masses. Dunham parameters are expressed as a series $Y_{kl} = Y_{kl}^0 + Y_{kl}^1$ with a zero-order term arising from the first-order WKB quantization and first-order terms linked to higher order WKB

quantization contributions and to corrections of Born-Oppenheimer approximation. First-order terms have a contribution to the value of the energy levels reduced by a factor of $\sim m_e/m_p$. Major contributions to the value of the energy levels are brought by $Y_{01}^0 \sim B_e$ and $Y_{10}^0 \sim \omega_e$ that approximate respectively rotational and vibrational intervals and by $Y_{02}^0 \sim -\omega_e x_e$ and $Y_{11}^0 \sim -\alpha_e$ that approximate respectively anharmonicity and rotation-vibration constant. Assuming that proton mass and neutron mass have similar variations, the sensitivity of the rovibrational energy to the fractional variation of μ is expressed as a series depending on the sensitivities of the Dunham parameters:

$$\begin{aligned} dE_{rv}/d(\ln\mu) &= \sum_{k,l} [dY_{kl}/d(\ln\mu)] (v+1/2)^k [J(J+1)]^l \\ dY_{kl}/d(\ln\mu) &= -U_{kl}\mu_r^{-(k/2+l)} [(k/2+l) + (k/2+l+1)\Delta_{H,kl} m_e/m_H + (k/2+l+1)\Delta_{Li,kl} m_e/m_{Li}] \end{aligned} \quad (3)$$

At the zero-order approximation (rigid rotor and harmonic oscillator), the sensitivity of the rovibrational energy is expressed as: $dE_{rv}/d(\ln\mu) \sim -B_e J(J+1) - 1/2\omega_e(v+1/2)$. The quadratic dependence with J and linear with v is the general mechanism to increase the absolute value of the sensitivity. Transitions couple rovibrational energy levels with different sensitivities according to dipole selection rules. The frequency f of a transition has a sensitivity, respectively a sensitivity coefficient to a fractional variation of μ expressed in terms of the higher state E_1 and lower state E_2 energies as:

$$\begin{aligned} df/d(\ln\mu) &= dE_1/d(\ln\mu) - dE_2/d(\ln\mu) \\ K &= d(\ln f)/d(\ln\mu) = [dE_1/d(\ln\mu) - dE_2/d(\ln\mu)] / (E_1 - E_2) \end{aligned} \quad (4)$$

Consider the overlapping of rotational manifolds at frequencies $f_{r1}(J',v')$, $f_{r2}(J'',v'')$ from different isotopomers or vibrational levels. Rotational frequencies are expressed at the first-order approximation as the sum of a pure rotation term and a rotation-vibration term $f_r = f_{rot} + f_{rot-vib}$ for which the sensitivity coefficients are respectively -1 and -1.5 . Rotational frequencies are proportional with an effective rotational constant. If the frequencies of the lowest transitions are such that $f_{r1}(J' = 0, v') < f_{r2}(J'' = 0, v'')$, near resonant transitions $f_{r1}(J', v') \sim f_{r2}(J'', v'')$ are reached as J' , J'' increase when a multiple of one effective rotational constant is by a multiple of the other effective rotational constant. The frequency splitting $f_{r12} = f_{r1} - f_{r2} > 0$ has a sensitivity coefficient expressed as:

$$K_r = d(\ln f_{r12})/d(\ln\mu) = -[l + 1/2(f_{rot-vib1} - f_{rot-vib2})/f_{r12}] \quad (5)$$

Near resonant transitions for which $f_{r12} \ll |f_{rot1} - f_{rot2}| \sim |f_{rot-vib1} - f_{rot-vib2}|$ yield a sensitivity coefficient enhanced by a half of the ratio between the difference of the rotational terms and the frequency splitting comparing to that of a pure rotational term.

Alternatively, consider the overlapping of rovibrational manifolds from different isotopomers or vibrational bands at frequencies $f_{rv1}(m',v')$, $f_{rv2}(m'',v'')$ where $m = -J$ for P branch transitions and $m = J + 1$ for R branch transitions of $v \rightarrow v + 1$ vibrational bands. Rovibrational frequencies are expressed at the zero-order approximation as the sum of a rotational term and a vibrational term $f_{rv} = f_r + f_v$ for which the sensitivity coefficients are respectively -1 and -0.5 . The frequencies of the transitions are such that $f_{rv1}(m' = 0, v') < f_{rv2}(m'' = 0, v'')$. Near resonant transitions are reached when $m' > 0$, $m'' > 0$ increase, $m' < 0$, $m'' < 0$ decrease, or $m' > 0$ increases and $m'' < 0$ decreases such that the frequency difference of the vibrational terms is by a linear combination with m' , m'' of the effective rotational constants. The frequency splitting $f_{rv12} = f_{rv1} - f_{rv2} > 0$ has a sensitivity coefficient expressed as:

$$K_{rv} = d(\ln f_{rv12})/d(\ln \mu) = -1/2 [1 + (f_{r1} - f_{r2})/f_{rv12}] \quad (6)$$

Near resonant transitions for which $f_{rv12} \ll |f_{r1} - f_{r2}| \sim |f_{v1} - f_{v2}|$ yield a sensitivity coefficient enhanced by the ratio between the difference of the vibrational terms and the frequency splitting comparing to that of a vibrational term.

Rovibrational energy depends on the reduced mass that can be significantly changed by isotopic substitution. Values of the Dunham parameters determined in [30] are plotted against the reduced mass of the isotopic species in Fig. 1. The curve displays the zero-order term dependence on the reduced mass. Significant shift of the parameters is demonstrated by isotopic substitution. First-order terms contribution shift slightly data points below the curve by a quantity depending on atomic masses. Energies of the lowest rovibrational levels have been calculated with equation (1) using isotopic lithium hydride parameters from [30] and plotted in Fig. 2. Quadratic dependence of the rotational energy yields pairs of near resonant levels for a given isotopomer with intermediate values of J although $\omega_e/B_e \sim 2 \times 10^2$. Direct measurement of the splitting by coupling the levels with a rovibrational transition is forbidden by dipole selection rules.

3. Results and discussion

Frequency and sensitivity of isotopic lithium hydride rotational and rovibrational transitions in the lowest vibrational levels have been calculated to a high degree of approximation with equations (1–4). The parameters used are 17 isotopically-independent Dunham parameters

with 7 dimensionless first-order correction terms determined by fitting rotational lines up to $J = 30$ in vibrational levels $v = 0 - 3$ measured with an accuracy of 15 MHz and rovibrational lines up to $J = 26$ in vibrational bands $v \rightarrow v + 1$ up to $v = 2$ measured with an accuracy <45 MHz [30]. This model reproduced experimental frequencies with an accuracy of 29 MHz and been used in calculations for transitions up to $J = 30$ and $v = 3$.

Uncertainty of the calculated frequency, respectively sensitivity is primarily determined by the uncertainties of the fitted parameters and is estimated as the quadratic sum of the relevant $\delta Y_{kl}(v + 1/2)^k [J(J + 1)]^l$ respectively $\delta(dY_{kl}/d(\ln\mu))(v + 1/2)^k [J(J + 1)]^l$ terms where the uncertainties δY_{kl} , $\delta(dY_{kl}/d(\ln\mu))$ are determined from equations (2–3). Uncertainty of the frequency splitting, respectively of the difference of sensitivities of two transitions is the quadratic sum of frequency, respectively sensitivity uncertainty of each transition. Fractional uncertainty of the sensitivity coefficient is the quadratic sum of fractional uncertainties of the frequency splitting and the difference of sensitivities. As a general rule, transitions with higher J , v have increased uncertainties. Contributions of higher-order terms neglected in the Dunham expansion are estimated with: $U_{kl} \sim U_{01}(U_{01}/U_{10})^{k+2(l-1)}$ [32] and lead to uncertainties that are by a factor of 4 for rovibrational transitions, respectively 40 for rotational transitions less than uncertainties determined by the parameters.

Let's consider an anchor rotational transition at $f_{r1}(v, J)$ in a lower vibrational level and the same transition of the same isotopomer probed in a higher vibrational level at $f_{r2}(v + n, J)$. The frequency splitting between these transitions defines the vibrational shift that is expressed at the first-order approximation as:

$$f_{r1}(v, J) - f_{r2}(v + n, J) = 2n\alpha_e(J + 1) \quad (7)$$

The sign of the rotation-vibration constant leads to a positive vibrational shift. For low J values it is considerably smaller than the frequency shift between successive rotational transitions that is the effective rotational interval:

$$f_{r1}(v, J) - f_{r1}(v, J - 1) = 2[B_e - \alpha_e(v + 1/2)] \quad (8)$$

Vibrational shift increases with J and near resonant transitions are found when it equals an even multiple of the effective rotational interval. Transitions $J = J_0 \rightarrow J_0 + 1$ in the vibrational level $v + 1$ and $J = J_0 - 1 \rightarrow J_0$ in the vibrational level v are resonant for an intermediate value of J_0 , as $B_e/\alpha_e \sim 40$. For $n = 2$ or 3 near resonant transitions are found at the lowest frequency for $J \sim J_0/n$. In addition, the increased vibrational shift yields near resonant transitions at higher frequency $J = J_k - k \rightarrow J_k - k + 1$ in the vibrational level v and $J = J_k \rightarrow J_k + 1$ in the

vibrational level $v + k$ for $J_k \sim kJ_0/n$ and $k = 2$ or 3 . Sensitivity of their frequency splitting to the variation of μ arises from different dependences of the vibrational shift and of the effective rotational interval on the variation of μ . Dependence on frequency of the sensitivity of the rotational transitions in the vibrational levels $v = 0$ and $v = 1$ for ${}^7\text{LiH}$ is plotted in Fig. 3 a. The sensitivity coefficient of a pair of transitions is the slope of the line defined by the corresponding data points. The extremum of the sensitivity coefficient is $-227.62(80)$ for the frequency splitting between the transitions $J = 23 \rightarrow 24$ in the vibrational level $v = 0$ and $J = 24 \rightarrow 25$ in the vibrational level $v = 1$. The sensitivity coefficient changes rapidly by varying each J by a unit around the previous values as it is shown in the inset. Although the frequency splitting is set positive, the sensitivity coefficient is positive or negative for lower, respectively higher J values, that is the frequency splitting increases, respectively decreases when the mass ratio constant increases.

The frequency shift between rotational transitions in different vibrational levels from isotopic molecules with the ratio of the reduced masses $r = \mu_1/\mu_2 < 1$ defines the isotopic shift expressed at the first-order approximation as:

$$f_{r1}(v, J) - f_{r2}(v+n, J) = 2[(1-r) - \alpha_{e1}/B_{e1}][v+1/2](1-r^{3/2}) - nr^{3/2} B_{e1}(J+1) \quad (9)$$

Near resonant transitions are found when the isotopic shift is equal to the frequency difference of rotational transitions of one isotopomer:

$$f_{r1}(v, J) - f_{r1}(v, J') = 2[1 - \alpha_{e1}/B_{e1}(v+1/2)]B_{e1}(J - J') \quad (10)$$

Consider the case of ${}^6\text{Li}/{}^7\text{Li}$ isotopic substitution where $1-r$ and $-\alpha_{e1}/B_{e1}$ terms have the same order of magnitude, opposite signs and values within a factor of 2. For a proper choice of v and n , the isotopic shift may be cancelled by the vibrational contribution. This mechanism allowed series of near resonant transitions $J = J \rightarrow J + 1$ in the vibrational levels $v = 0$ of ${}^7\text{LiD}$ and $v = 2$ of ${}^6\text{LiD}$ with a maximum sensitivity coefficient of $-3.7105(1)$ for $J = 0$. The splitting increases with J from its lowest value of $2.08(6)$ GHz for $J = 0$ transitions to $94.7(6)$ GHz for $J = 29$ transitions while the sensitivity coefficient increases slowly to $-2.931(3)$ as shown in Fig. 3 b. The pairs of transitions at low J values are relevant for astrophysical observations. The sensitivity coefficient is comparable with that of the ammonia inversion frequency [5] and two orders of magnitude higher than that of H_2 Lyman and Werner transitions [4]. The mechanism is general and similar dependences have been identified for other isotopic species, for example transitions $J = J \rightarrow J + 1$ in the vibrational levels $v = 0$ of ${}^7\text{LiH}$ and $v = 1$ of ${}^6\text{LiH}$ that displays a splitting at $J = 0$ of $3.926(2)$ GHz with a sensitivity coefficient of $-2.66867(2)$.

Alternatively, the isotopic shift for intermediate J may equal a few effective rotational intervals as discussed previously. This mechanism leads for example to extremums of the sensitivity coefficient of near resonant transitions $J = 17 \rightarrow 18$ in the vibrational level $v = 1$ of ${}^7\text{LiH}$ and $J = 16 \rightarrow 17$ in the vibrational level $v=0$ of ${}^6\text{LiH}$ of 53.618(1), respectively $J = 26 \rightarrow 27$ in the vibrational level $v=0$ of ${}^6\text{LiH}$ and $J = 28 \rightarrow 29$ in the vibrational level $v = 1$ of ${}^7\text{LiH}$ of -144(5) as shown in Fig. 3 c. Consider the case of H/D isotopic substitution where $1 - r \sim 1/2$ leads to an isotopic shift that is about a half of the rotational frequency. Increased isotopic shift allows to reach near resonant transitions at a lower J such as $J \sim 2J'$. This mechanism leads to the pair of transitions $J = 7 \rightarrow 8$ in the vibrational level $v = 0$ of ${}^7\text{LiH}$ and $J = 14 \rightarrow 15$ in the vibrational level $v = 2$ of ${}^7\text{LiD}$ with a sensitivity coefficient of 806(4) as shown in Fig. 3 a.

Frequency of a rovibrational transition in the $v = v \rightarrow v + 1$ vibrational band is expressed at the first-order approximation by a single formula depending on parameter $m = m(J)$ defined previously as:

$$f_{rv}(v,m) = \omega_e - 2\omega_e x_e(v+1) + 2[B_e - \alpha_e(v+1)]m - \alpha_e m^2 \quad (11)$$

The rovibrational frequency increases with m, reach a maximum for $m_{\max} = B_e/\alpha_e - (v + 1)$ and decreases. The expression derived for the sensitivity of the rovibrational frequency is:

$$df_{rv}(v,m)/d(\ln\mu) = -[\omega_e/2 - 2\omega_e x_e(v+1) + [2B_e - 3\alpha_e(v+1)]m - 3/2\alpha_e m^2] \quad (12)$$

The sensitivity decreases with m to reach a minimum for $m_{s,\min} = 2B_e/3\alpha_e - (v + 1)$ and increases. For the lowest vibrational levels $m_{s,\min} \sim 2/3m_{\max}$. This dependence with m of the rovibrational frequency provides a mechanism to reach pairs of near resonant transitions in the R branches at $m \sim m_{\max}$. Indeed, ${}^7\text{LiH}$ rovibrational transitions in the $v = 0 \rightarrow 1$ band reach the highest frequency at $m_{\max} = 23$ while the extremum of sensitivity is at $m_{s,\min} = 15$ (shown in Fig. 4). R(23) and R(24) transitions have a frequency splitting of 1(2) GHz and a sensitivity coefficient of -227.6(3) (Fig. 4 (a0)). Frequency splitting and sensitivity coefficient of R(23 - Δm) and R(24 + Δm) transitions increases, respectively decreases with Δm and reaches 9(30) GHz, respectively -284(8) for R(29) and R(18) transitions (Fig. 4 (a1) to (a5) and inset).

Consider an anchor rovibrational transition at $f_{rv1}(v,m)$ from a lower vibrational level and the same transition from an upper vibrational level at $f_{rv2}(v + n,m)$. The vibrational shift is expressed at the first-order approximation as:

$$f_{rv1}(v, m) - f_{rv2}(v + n, m) = 2n\alpha_e(\omega_e x_e / \alpha_e + m) \quad (13)$$

Values of the anharmonicity and rotation-vibration constant lead to a positive vibrational shift. As $\omega_e x_e / \alpha_e \sim 3B_e / \alpha_e \sim 140$, the vibrational shift increases slightly with m around an even multiple of three times the rotational interval and it has to be compared with the frequency shift between rovibrational transitions:

$$f_{rv1}(v, m) - f_{rv1}(v, m') = 2(m - m') \times \alpha_e [B_e / \alpha_e - (v + 1) - (m + m')/2] \quad (14)$$

Pairs of near resonant transitions from P and R branches reached for small values of m, m' such that $m - m' = n$ displays a small sensitivity coefficient because of the same dependence on the variation of μ of B_e and $\omega_e x_e$. Near resonant transitions are found in P branches for a small value of $m - m' > 0$ and intermediate m, m' values, respectively in R branches for high m and low m' values. For ${}^7\text{LiH}$, the most sensitive pairs of transitions are P(16) of $v = 2 \rightarrow 3$ and P(18) of $v = 1 \rightarrow 2$ with a sensitivity coefficient of $-305.059(8)$ (Fig. 4 (a)), respectively R(26) of $v = 3 \rightarrow 4$ and R(10) of $v = 2 \rightarrow 3$ with a sensitivity coefficient of $4705.40(5)$ (Fig. 4 (b)).

The isotopic shift of rovibrational transitions is expressed at the first-order approximation as:

$$f_{rv1}(v, m) - f_{rv2}(v + n, m) = \omega_e (1 - r^{1/2}) - 2\omega_e x_e [(v + 1)(1 - r) - nr] + 2[B_e(1 - r) - \alpha_e [(1 - r^{3/2})(v + 1) - nr^{3/2}]]m - \alpha_e (1 - r^{3/2})m^2 \quad (15)$$

The isotopic shift displays additional terms depending on ω_e, B_e that allows to span a broader frequency range than that of the vibrational shift. Consider the case of ${}^6\text{Li}/{}^7\text{Li}$ isotopic substitution for which $\omega_e(1 - r^{1/2}) \sim 2B_e$. Near resonant transitions are reached at low m, m', v as the isotopic shift that is about two times the rotational interval equals the frequency shift given by equation (14). The most sensitive pair of transitions is R(0) of ${}^6\text{LiH}$ and R(1) of ${}^7\text{LiH}$ in the $v = 0 \rightarrow 1$ band that displays a frequency splitting of $345(3)$ MHz with a sensitivity coefficient of $-585.391\ 84(6)$. Near resonant transitions can be reached at higher n, v in P branches for intermediate m, m' and low $m - m'$, respectively in R branches for high m and low m' as noted previously. Pairs of ${}^6\text{LiD}/{}^7\text{LiD}$ transitions lead to extremums of the sensitivity coefficients: $4\ 578.40(1)$ for P(21) of ${}^6\text{LiD}$ $v = 0 \rightarrow 1$ band and P(20) of ${}^7\text{LiD}$ $v = 0 \rightarrow 1$ band (Fig. 4 (c)), respectively $26\ 949.208(1)$ for R(16) of ${}^7\text{LiD}$ $v = 3 \rightarrow 4$ band and R(0) of ${}^6\text{LiD}$ $v = 0 \rightarrow 1$ band (Fig. 4 (d)). Consider the case of H/D isotopic substitution for which $\omega_e(1 - r^{1/2}) \sim 50B_e$. Near resonant transitions are reached in P branches respectively in P and R branches for intermediate m, m' . In this case, the isotopic shift is sensibly higher than frequency splittings of near resonant transitions lower than the rotational interval. This

mechanism push at the limits the values of the sensitivity coefficients: 73 748.47(1) for P(21) of ${}^7\text{LiH } v = 3 \rightarrow 4$ band and P(15) of ${}^7\text{LiD } v = 0 \rightarrow 1$ band (Fig. 4 (e)), respectively -21 672(137) for P(13) of ${}^7\text{LiD } v = 1 \rightarrow 2$ band and P(25) of ${}^6\text{LiH } v = 1 \rightarrow 2$ band (Fig. 4 (f)).

Consider the comparison of frequency intervals between transitions at $f_{a1,a2}$ with sensitivity coefficients $K_{a1,a2}$ and transitions at $f_{b1,b2}$ with sensitivity coefficients $K_{b1,b2}$. Transitions are detected in an astrophysical object with redshift z_0 at radial velocities $V_{a1,a2}, V_{b1,b2}$. The fractional variation of the ratio of the measured frequency splittings f_{a12}/f_{b12} due to the variation of μ is expressed as:

$$\begin{aligned} \Delta(f_{a12}/f_{b12})/(f_{a12}/f_{b12}) &= (K_{a12} - K_{b12})\Delta\mu/\mu \\ K_{a,b12} &= (f_{a1,b1}K_{a1,b1} - f_{a2,b2}K_{a2,b2})/(f_{a1,b1} - f_{a2,b2}) \end{aligned} \quad (16)$$

Relative effects are enhanced by comparing pairs of transitions with different sensitivity coefficients. Any frequency shift of the molecular spectra is linked to a radial velocity shift:

$$\begin{aligned} \Delta(f_{a12}/f_{b12})/(f_{a12}/f_{b12}) &= (V_{a,eff} - V_{b,eff})/c \\ V_{a,b,eff} &= (f_{a1,b1}V_{a1,b1} - f_{a2,b2}V_{a2,b2})/(f_{a1,b1} - f_{a2,b2}) \end{aligned} \quad (17)$$

where an effective radial velocity associated to the frequency splitting between near resonant lines is defined as the weighted difference of the radial velocities of each line. Comparison between two frequency intervals with different sensitivity coefficients using equations (16–17) put constraints to the fractional variation of μ :

$$\Delta\mu/\mu = (V_{a,eff} - V_{b,eff})/[c(K_{a12} - K_{b12})] \quad (18)$$

The signature of the variation of μ is an apparent shift between the effective velocities of frequency intervals with different sensitivity coefficients. The approach is similar to the ammonia method [5] for searching a possible variation of μ from a shift between the radial velocity of ammonia inversion lines with $K = -4.46$ and the average radial velocity of rotational lines with $K = -1$. Shift may be hidden when the molecular lines are observed with multiple velocity components due to the structure of the transition or of the molecular cloud. The alternative was a simultaneous fitting of all free parameters of the velocity components including the variation of μ that shifts the scale of radial velocities [33]. Difference between sensitivity coefficients of the transitions was neglected in the comparison with the average radial velocity of rotational lines or by assuming the same velocity components distribution for different transitions of a molecule. The comparison of frequency intervals accounts for the sensitivity coefficient of each transition and allows to put constraints for a variation of μ with sensitivity coefficients and radial velocities in an extended range of values than those of the transitions. Contributions from the Doppler profile, the structure of the transition or of the

molecular cloud to the velocity profile lead to a velocity uncertainty for each line proportional with its linewidth. Uncertainty of the effective velocity for near resonant transitions increases as the inverse of the frequency splitting. Uncertainty of the variation of μ is determined by contributions of the sensitivity coefficients and the associate frequency splittings. Potential enhancement of the sensitivity to the variation of μ allowed by higher sensitivity coefficients of near resonant transitions is reduced by the small contributions of frequency splittings. As each line have a different sensitivity and accuracy, statistical analysis of the measurements may lead to tighter constraints on the variation of μ from the comparison of splittings between near resonant lines with accurate effective velocities than that from the comparison of individual lines with high sensitivity coefficient but lower accuracy.

The first comparison of frequency intervals between rotational transitions of diatomic molecules detected in the spectrum of B0218+357 is reported in Table 1. Only line $J = 0 \rightarrow 1$ of ${}^7\text{LiH}$ in $v = 0$ vibrational level has been detected at a velocity $v_{\text{al}} = 5$ km/s with an instrumental uncertainty of $\Delta v_{\text{al}} = 1.1$ km/s [22]. Frequency intervals are defined to the detected isotopic CO lines [34] that are fitted here with Gaussian profiles with velocity components, Doppler widths and optical depths. Line ${}^{13}\text{CO } J = 1 \rightarrow 2$ has been fitted with a single velocity component. Line ${}^{12}\text{CO } J = 1 \rightarrow 2$ has been fitted with two velocity components and the unweighted average radial velocity is considered. Dunham parameters for isotopic CO [35] allow to calculate sensitivity coefficients and effective radial velocities for the frequency intervals. Inversion lines of ammonia reported in [36] with two velocity components are used as references with higher sensitivity coefficient and the unweighted average radial velocity is considered. Each frequency interval defined by LiH/CO transitions is compared with an ammonia transition to put constraints on the variation of μ . The unweighted average of the results is $\Delta\mu/\mu = (5.06 \pm 3.67) \times 10^{-6}$. This estimation may be improved by a comparison of frequency intervals defined with rotational transitions of other molecules detected in B0218+357. The use of small frequency splittings is associated with increased uncertainties on both sensitivity coefficients and effective radial velocities thus reducing statistical contribution of this data to the estimation. Identification of series of pairs of transitions with an enhanced sensitivity coefficient varying slowly with their frequency splitting seems more appropriate and may drive the search for new data.

4. Conclusion

This article presents calculations of the sensitivity of isotopic lithium hydride rotational and rovibrational transitions in its electronic ground state to a variation of the proton-to-electron mass ratio within the Dunham expansion formalism. It demonstrates that the frequency splitting between two near resonant transitions is highly sensitive to a variation of μ . At the lowest approximation order, such resonances arise from the cancellation of effective rotational intervals with frequency shifts associated to the rotation-vibration interaction or isotope effect for the rotational transitions, respectively with frequency shifts associated to the anharmonicity and isotope effect for the rovibrational transitions. Terms that cancel have different dependences on the variation of μ leading to an enhancement of the sensitivity coefficient of the frequency splitting to that of a transition. Taking into account rotational structure of the energy levels allows to identify pairs of transitions in the range of low to intermediate J of the lowest vibrational levels that is complementary to the approach based on vibrational energy levels [15–17]. Calculations allow the comparison of frequency intervals defined between molecular lines detected in an astrophysical object. The use of frequency intervals instead of transitions [5] may increase the contribution of relative effects to the variation of μ by addressing an extended range of sensitivity coefficients and effective radial velocities. Frequency intervals defined between LiH and isotopic CO rotational lines are compared with ammonia lines detected in the microwave spectra of B0218+357 quasar to put constraints to a variation of μ .

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Figure captions

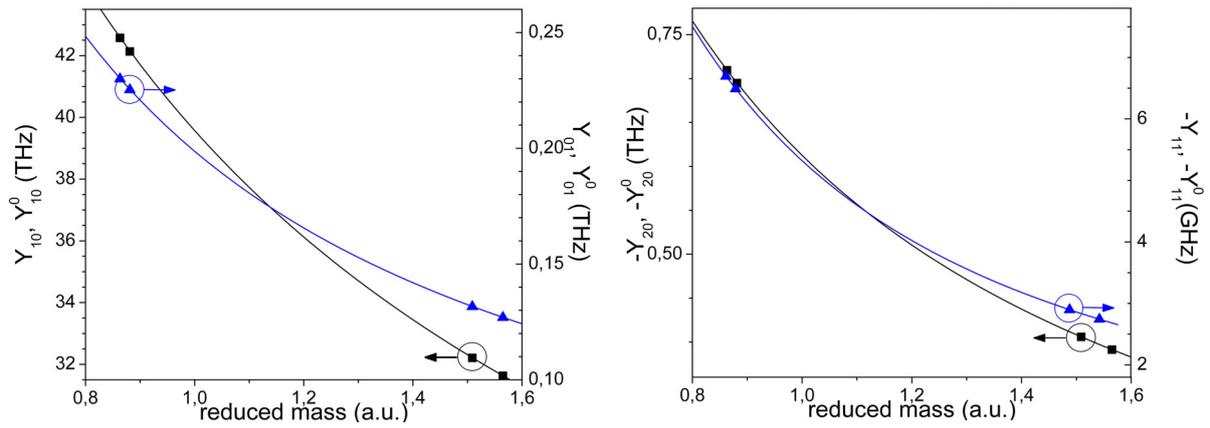


Fig. 1. Dependence of Dunham parameters on the isotopomer reduced mass.

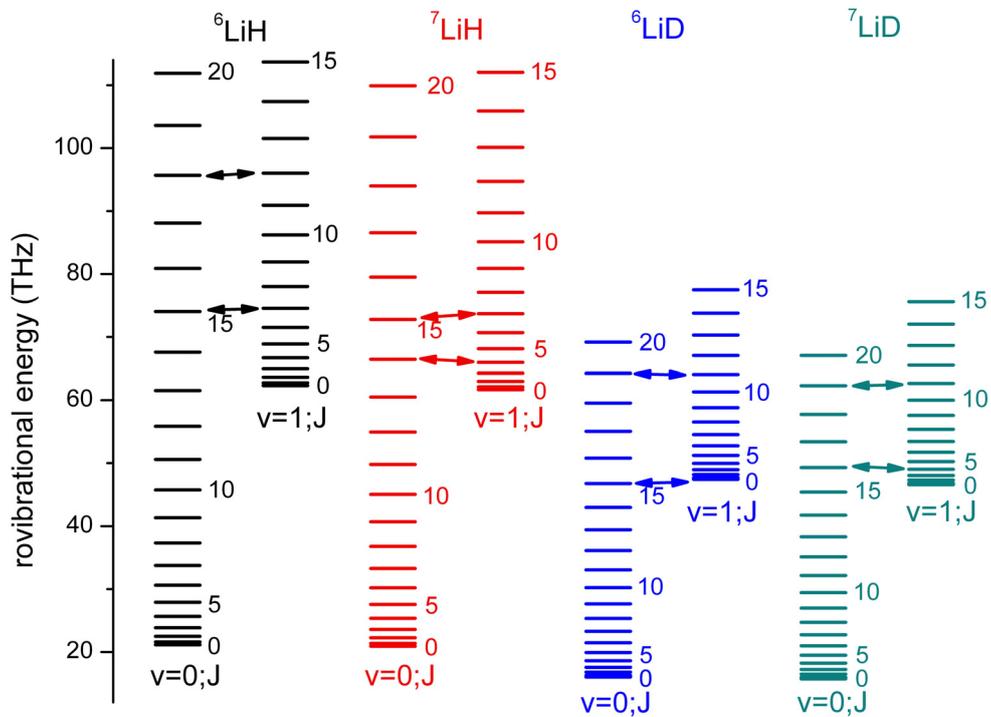


Fig. 2. Energy of isotopic lithium hydride rovibrational levels. Arrows indicate some pairs of near resonant energy levels.

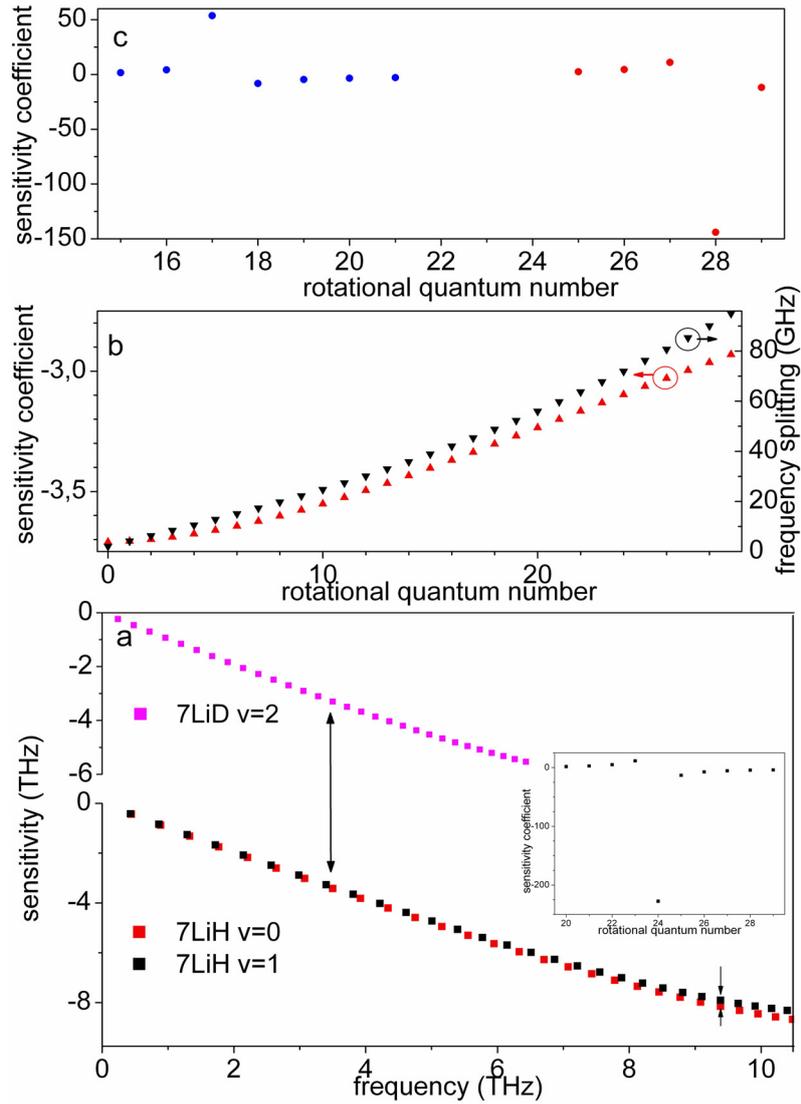


Fig. 3. a. Sensitivity of the rotational transition against the rotational frequency for lithium hydride isotopomers in selected vibrational levels. Inset: dependence on J of the sensitivity coefficient for ${}^7\text{LiH}$ transitions $J \rightarrow J+1$ in the vibrational level $\nu=0$ and $J+1 \rightarrow J+2$ in the vibrational level $\nu=1$. Arrows indicate pairs of transitions discussed in the text.

b. Dependence on J of the sensitivity coefficient and the frequency splitting between the transitions $J \rightarrow J+1$ in the vibrational levels $\nu=0$ of ${}^7\text{LiD}$ and $\nu=2$ of ${}^6\text{LiD}$.

c. Dependence on J of the sensitivity coefficient of the frequency splitting between the transitions $J \rightarrow J+1$ in the vibrational level $\nu=1$ of ${}^7\text{LiH}$ and $J-1 \rightarrow J$ in the vibrational level $\nu=0$ of ${}^6\text{LiH}$ (red points), respectively $J \rightarrow J+1$ in the vibrational level $\nu=1$ of ${}^7\text{LiH}$ and $J-2 \rightarrow J-1$ in the vibrational level $\nu=0$ of ${}^6\text{LiH}$ (blue points).

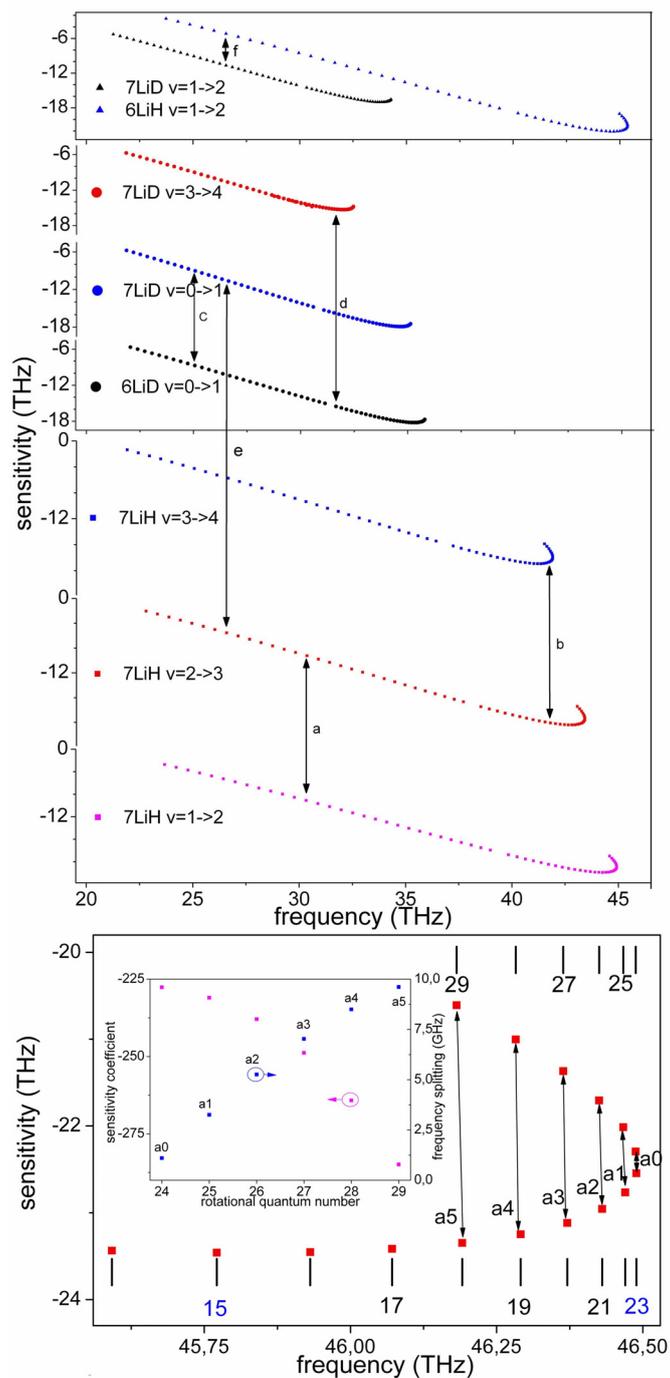


Fig. 4. Sensitivity of rovibrational transition against rovibrational frequency for lithium hydride isotopomers in selected vibrational bands. Arrows indicate pairs of near resonant transitions discussed in the text. Inset: Dependence on J of the sensitivity coefficient and frequency splitting between the transitions $R(J)$ and $R(J - 2\Delta m - 1)$ for $\Delta m = 0 - 5$ of ${}^7\text{LiH}$ $v = 0 \rightarrow 1$ band.

Table captions

Table 1. Comparison of frequency intervals between lithium hydride and isotopic CO rotational lines with ammonia inversion lines detected in the microwave spectra of B0218+357 quasar.

Species	Transitions	Sensitivity	Radial velocity (km/s)
${}^7\text{LiH}/{}^{13}\text{CO}$	$J = 0 \rightarrow 1 / J = 1 \rightarrow 2$	-0.9858233(5)	4.13 ± 2.20
${}^7\text{LiH}/{}^{12}\text{CO}$	$J = 0 \rightarrow 1 / J = 1 \rightarrow 2$	-0.9853287(5)	6.18 ± 2.75
${}^{14}\text{NH}_3$	J, K = 1, 1	-4.46	0.65 ± 1.37
${}^{14}\text{NH}_3$	J, K = 2, 2	-4.46	0.7 ± 1.52
${}^{14}\text{NH}_3$	J, K = 3, 3	-4.46	-1.7 ± 2.91