# Implementation of Morse potential for approximation of vibrational terms of diatomic molecules

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We analysed the problem of approximation of the potential function of a diatomic molecule by a Morse model function with constant anharmonicity $vx$ using the Birge−Sponer extrapolation. The analysis of the approximations used in the derivation of the Morse equation shows that the solution of this problem is ambiguous. A scheme for optimizing the selection of initial parameters is proposed, which is illustrated by examples taken from the literature. The advantages of delineation of anharmonicity in the excitation of vibrational levels by deviations of the value $vx$ from the constant value according to Morse are demonstrated. An attempt is made to use the dimensionless anharmonicity parameter $x^*$ as a universal characteristic of the shape features of the electronic term of the molecule.

**Keywords:** Morse potential, diatomic molecule, Birge−Sponer extrapolation, anharmonicity, electronic terms, vibrational structure.

In the courses of molecular spectroscopy, the Morse model potential is traditionally mentioned always in the presentation of the principles of the formation of the vibrational structure of the spectra of simple molecules and methods for the approximate estimation of the chemical bond energy. Despite a very rough approximation and often only semi-quantitative agreement with experiment, this function is preserved in curricula and textbooks until recently [1–7], and its diverse applications and modifications are developed in the scientific literature [ 8–12]. The main reason for the continued popularity of the Morse function is the integrability of the Schrödinger equation with such a potential and the abundance of objectives, in which there is a high need for an approximate estimating solution that allows further targeted elaboration. Due to its simplicity and clarity, the Morse function is easily caught on to students, but at the same time patterns are formed in the educational system that cramp evolutionary development. Let's discuss an important detail that has not been fully realized in the literature for almost a hundred years of using this potential — the possibility of varying the parameters of function when approximating real terms and on the development of the methodology for describing anharmonicity.

## Alternative approximations of the real electronic term

To approximate the real electronic term by the Morse equation [13]

$$U(r) = D_e \left[ 1 - e^{-a(r-r_e)} \right]^2 \qquad (1)$$

it is necessary to specify three values of the parameters $D_e$, $r_e$ and „$a$". The meaning of $D_e$ (the depth of the potential well) and $r_e$ (the position of the minimum of the potential curve minimum) is clear, and the constant „$a$", which determines the width of the potential energy well and the very existence of the dissociation limit, is included in the coefficients of the solution of the Schrödinger equation with this potential:

$$G(v) = v_e \left( v + \frac{1}{2} \right) - v_e x_e \left( v + \frac{1}{2} \right)^2, \qquad (2)$$

where

$$v_e = a(2D_e/M\hbar)^{1/2}, \quad v_e x_e = \hbar a^2/2M, \qquad (3)$$

$v_e$ is harmonic frequency, $M$ is reduced molecular mass, $v_e x_e$ is anharmonicity coefficient. Hence $a = 2\pi v_e (M/2D_e)^{1/2}$. It follows approximately from (3) that

$$D_e = v_e^2/4v_e x_e. \qquad (4)$$

This last relation allows use of the anharmonicity $v_e x_e$ or only $x_e$ instead of $D_e$ to determine „$a$" and just this option is suggested by Morse as the final result of his work (article [13] is named „Diatomic molecules according to the wave mechanics. II. Vibrational levels.") and uses it to determine the dissociation energy of diatomic molecules series by the extrapolation method. In the future, when using the Morse equation (1), the authors most often indicate the first option. It is also often given in textbooks and monographs [2–7]. Sometimes the authors give both options, mentioning their equivalence, for example in [14,15], although the expression (4) is laden with a systematic error, the nature of which requires mentioning, since it inevitably leads to two possible values of the parameter „$a$".

The first systematic error lies in the definition of the depth of the potential energy well $D_e$, which Morse takes equal to the position of the last vibrational level $v_{\max}$, and thus the value $D_e$ turns out to be underestimated by a value slightly less than the last vibrational quantum. From (2) it formally follows

$$v_{\max} = v_e / 2 v_e x_e - 1/2, \qquad (5)$$

but the integer part use introduces the second systematic error. These considerations are not explicitly mentioned in the literature, although it follows that the parameter „$a$", expressed in terms of the anharmonicity $v_e x_e$ in (4), is underestimated due to the systematic error (5). This leads to an overestimation of $D_e$ and, possibly, to an overestimation of the number of vibrational levels.

As a specific example, we approximated the potential curve with a vibrational structure for a hydrogen molecule in the ground electronic state, using two sets of parameters, including either $D_e$ or $x_e$, using literature data. In the first case, a picture was obtained similar to the scheme of Fig. 48 in the book [7], with the difference that the real vibrational levels in the upper part of the potential energy well converge much faster than it follows from the anharmonicity constancy condition, the number of levels increased from 14 to 16. This is natural, since in both cases the approximation is not very effective in the upper part of the potential, above $30\,000\,\mathrm{cm}^{-1}$ (approximately 20% of $D_e$), due to different asymptotics of the real and Morse curves. In the second case, the initial value of anharmonicity $x_e$, calculated from the experimental values of the first vibrational frequencies, decreased, and as a result, the position of the vibrational levels was better reproduced in the lower part of the well to almost $30\,000\,\mathrm{cm}^{-1}$. But the position of the asymptote increased by more than $3000\,\mathrm{cm}^{-1}$, and the number of vibrational levels increased to 18. It follows that the initial set of levels, including anharmonicity, is preferable in cases where reproducibility in the lower part of the potential energy well is important, but the dissociation energy is then extrapolated very roughly. If the dissociation energy is known, the first-type approximation makes it possible to obtain the frequency values and wave functions of the states in a wider range, but with somewhat less accuracy. Add that just this approach was long before and widely used in the theoretical study of the dynamic interaction of strong laser radiation with matter, when pumping over the vibrational degrees of freedom of the molecule occurs up to dissociation and transition to a continuous spectrum [16–18]. In these cases, it is more important to know the dissociation energy more accurately than the ordering law of the eigenfrequencies of the anharmonic oscillator.

To calculate the anharmonicity coefficient $x_e$ it is sufficient to know the position of the first three vibrational levels of real molecule, but if a larger number of them is known, new possibilities appear. The system of equations used to select $x_e$ value (and value $v_e$ simultaneously associated with it) becomes redundant, and the solution optimization may be due to the specifics of the problem.

First, by averaging the data over the frequencies of all known states, one can obtain a Morse approximation of the actual potential curve over a wide possible energy range, although with an inevitable loss of accuracy for high levels. Secondly, for some problems, there may be a need for an optimal description of a certain group of excited vibrational states that does not include one or more of the lowest states, and then it is advisable to determine the anharmonicity coefficient by averaging the data over the frequencies of precisely these states. Thirdly, experience shows that the lower levels often behave abnormally, i.e. go away more slowly than the higher ones, and this leads to an implausible description of both the entire subsequent vibrational structure and the value of the bond energy. We carried out such construction for the ground state of the oxygen molecule, the vibrational frequencies of which were calculated with high accuracy. The constants $v_e x_e$ were averaged over the intervals $v = 0-3$ and $v = 0-20$. The second option well reproduces the position of the levels i.e. frequency deviations in the section of about 3/4 of the depth of the potential energy well lie within $1-2\,\mathrm{cm}^{-1}$. In the first option the deviations are much larger, mainly due to the mentioned anomaly in the lower part of the well. Thus, we can assume that the Morse problem has a much larger number of solutions than two. Additionally, choosing the anharmonicity value $x_e$ such that to find $D_e$ from (4), we assume by default that the value $v_e$ in (4) is the harmonic frequency characteristic of the parabolic potential (Hooke's law [1], formula (20.100)). But for a real oscillator the position of all vibrational levels, including the zero one, depends on the anharmonicity, and considering (2) as an approximation equation, we give the values $v_e$ and $v_e x_e$ the meaning of adjustable coefficients only. In this case, of course, the relation (20.84) in [1] is satisfied. Hence, it follows that $v_e x_e$ can be varied both due to $x_e$ and $v_e$, or both, if, according to the conditions of the problem, the coefficient $x_e$ must satisfy some additional requirements.

## Empirical characteristic of anharmonicity

When processing experimental data, the Burge−Shponer extrapolation is of great virtue, based on an approximately linear empirical dependence of the differences between neighboring levels on the vibrational quantum number for the lower levels of series of diatomic molecules [19,20]:

$$\Delta G(v + 1/2) \equiv G(v) - G(v - 1). \qquad (6)$$

In the coordinates $\Delta G$, $v + 1/2$, the points are approximated by a straight line, whose extrapolation to the intersection with the abscissa axis allows one to obtain an approximate estimate of the molecular dissociation energy ([1], Fig. 20.9). A more detailed discussion is given in the useful paper [21]. In these coordinates, equation (6) for the Morse oscillator is strictly satisfied, the points in the Burge−Shponer coordinates lie on a straight line, the slope of which is determined by the anharmonicity value. The sign and
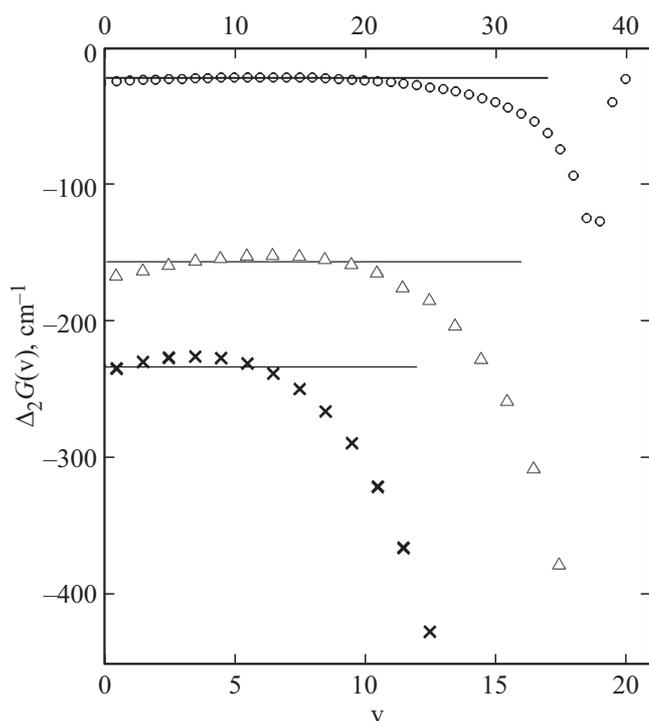
**Figure 1.** Second differences of the vibrational level energies vs. vibrational quantum number $F(v) = 2v_e x^*$ (equation (2), (7)) for hydrogen molecules $H_2$ (crosses) according to [23], and hydrogen fluoride HF (triangles) [24] (lower abscissa), as well as oxygen $O_2$ (circles) [25] (upper abscissa). Horizontal lines are drawn for each molecule at a level corresponding to the values of the anharmonicity constant, which follow from the Morse equation: $-234.5$, $-157.6$, $-23.31$ cm$^{-1}$ (see text).

absolute value of deviations from this straight line reflect the specifics of a real molecule, its individuality, and it makes sense to use the second differences, i.e., function

$$\Delta_2 G(v) \equiv \Delta G(v) - \Delta G(v - 1) = F(v) \qquad (7)$$

for the empirical systematics of the vibrational levels of the diatomic molecule. We plotted such dependences for several molecules, for which there are reliable values for a set of vibrational frequencies, experimental or calculated. Among other things, we chose „abnormal" terms that experience breaks due to non-intersections, which are analyzed in the paper of McCoy [22], who proposed the original quantum-mechanical approach to the Morse analysis of vibrational structure (see below). In coordinates (7) the Morse oscillator is represented by a set of points lying on a horizontal line in the negative half-plane. For ordinary terms the points are located near this straight line and (almost) monotonously move down, at first slowly, and then with acceleration approaching the asymptote, which indicates the increasing of anharmonicity. Fig. 1 shows examples of dependence (7) for the main electronic term of $H_2$, HF, and $O_2$ molecules. The anharmonicity values $v_e x_e$ were calculated so that the Morse condition was satisfactorily satisfied in the central part of the term. For oxygen,

for example, as mentioned above, the real values were averaged over the interval $v = 0-20$. The horizontal straight lines show $2v_e x$ value, which describes the position of the vibrational levels of the approximated Morse oscillator; points are not shown.

In a certain region near the asymptote, the concept of anharmonicity loses its meaning due to the dominance of the Van der Waals interaction between atoms, and we will not discuss it, and the first levels sometimes behave unexpectedly. For the ground term of hydrogen the points in the interval $v = 1-5$ move upward, i.e. the anharmonicity decreases, and then the anharmonicity increases rapidly up to the asymptote. This anomaly is almost invisible in the Burge–Shponer coordinates, but Gaydon briefly mentioned it in the book [20] (p. 108), and perhaps this is how the real potential curve deviates from the Morse potential, marked with a dotted line at the bottom of the curve in Fig. 48 in Herzberg book [7] on p. 76. The dependence $F(v)$ for the oxygen molecule is almost normal, although a weakly shown anomaly of this type in the region $v = 1-15$ is beyond dispute. Finally, for HF and DF molecules this anomaly is significant, but located in the middle part of the potential. We will discuss these molecules in more detail below. In general, for normal electronic terms the dependence $F(v)$ quantitatively reflects the deviation of the vibrational levels of the real term from its Morse approximation, which is shown in the diagram by horizontal line. Also Fig. 1 shows the interval $\Delta v$, in which the averaging was carried out to determine the initial value of $2v_e x$. Besides, for terms with a break in Fig. 1 it is possible to see a section, where ramp change in anharmonicity occurs. In more complicated cases described by McCoy in [22] (the terms $E^1\Sigma_g^+$ $Li_2$ and $X^1\Sigma_g^+$ $Be_2$), strong interaction in the region of intersection of diabatic terms manifests itself in a sharp jump in the anharmonicity constant of the resonant type, and in this case one can see some parallelism with its data. We believe that the analysis of the second differences $F(v)$, may be in combination with McCoy's approach, could make it possible to formulate useful diagnostic criteria for the shape of the electronic terms of simple molecules.

## Universal dimensionless anharmonicity scale

With the accumulation of such data, there is a need for their generalization, when the anharmonicity value would be universal, independent of the oscillation frequency. That is, there is a need to analyze the possibility of using the dimensionless parameter $x^*$ as a descriptor of the potential form. If we introduce the energy of vibrational levels $E$ in the form $E = G(v) - D_e$, taking the asymptote as zero, then the dependence $x^*(E)$ (its experimental realization is reflected by the function $F(v)$), which characterizes the anharmonicity deviations from the constant Morse value, could possibly serve as the next approximation for a
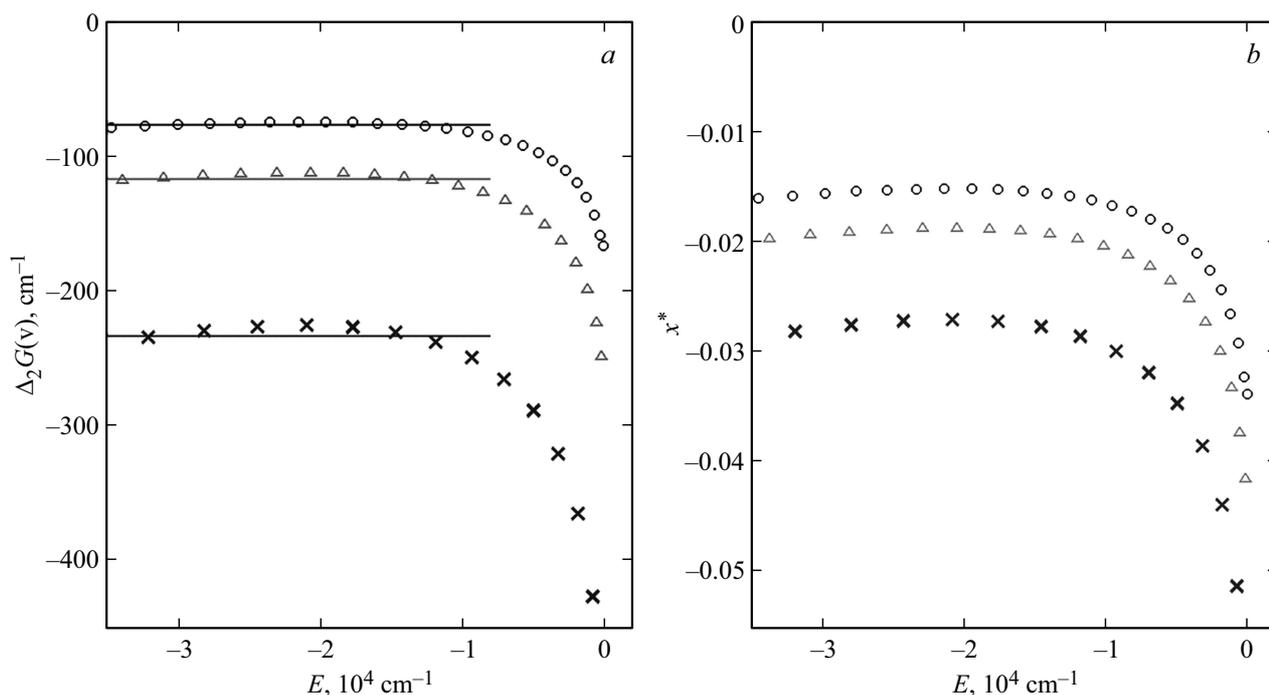
**Figure 2.** Comparison of the second differences $F(v)$ ($a$) and the reduced anharmonicity $x^*(E)$ ($b$) vs. the energy of vibrational levels $E$ for vibrational frequencies of molecules $H_2$ (crosses), $D_2$ (triangles), $T_2$ (circles) according to [23]. The quantities $\Delta_2 G(v) \equiv G(v) - \Delta G(v-1) = 2v_e x^*(v)$ and $x^*(v) = 2v_e x^*(v)/2v_e$ are calculated by the formula (7).
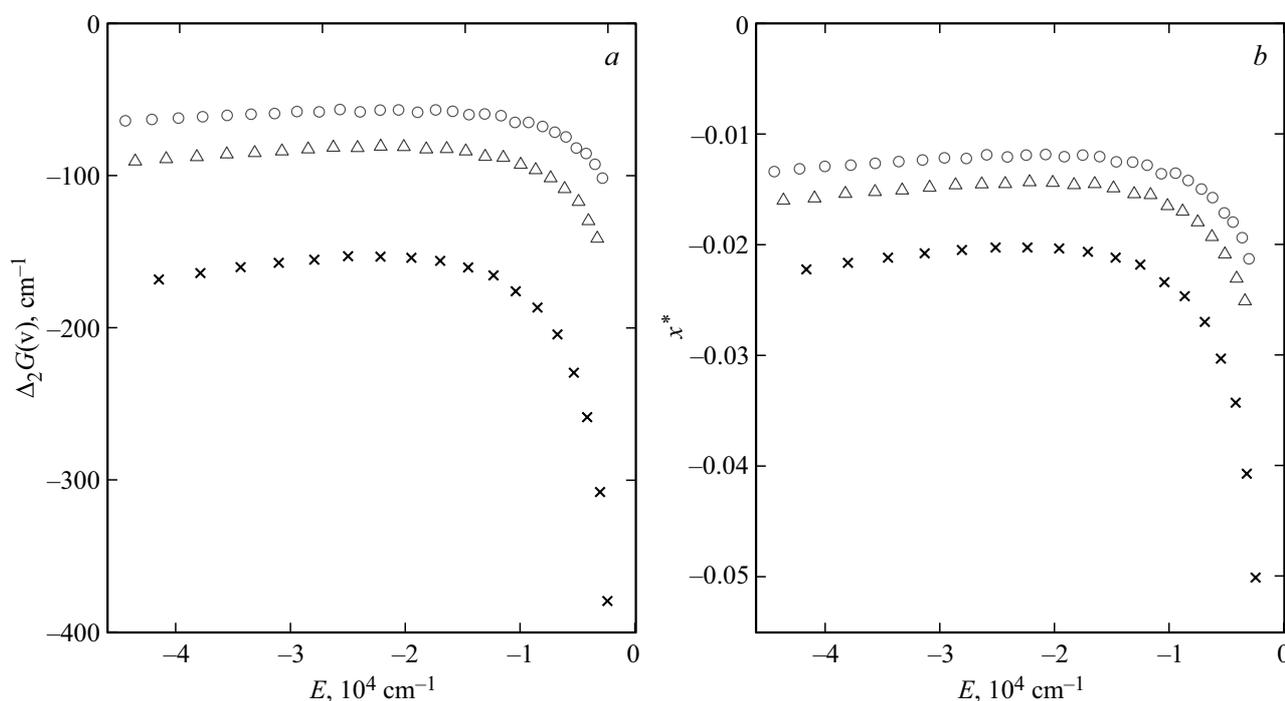


**Figure 3.** Comparison of the second differences $F(v)$ ($a$) and the reduced anharmonicity $x^*(E)$ ($b$) vs. the energy of vibrational levels $E$ for vibrational frequencies of molecules HF (crosses), DF (triangles), TF (circles) according to [24]. The calculations were carried out using the same formulas as in Fig. 2.

qualitative, and in favorable circumstances, semiquantitative characterization of the features of the potential type. At the first stage, it is important to compare the functions $x^*(E)$, if

possible, for several isotopic forms of the same molecule in order to find out how well the adiabaticity condition manifests itself in the behavior of this function, i.e., the
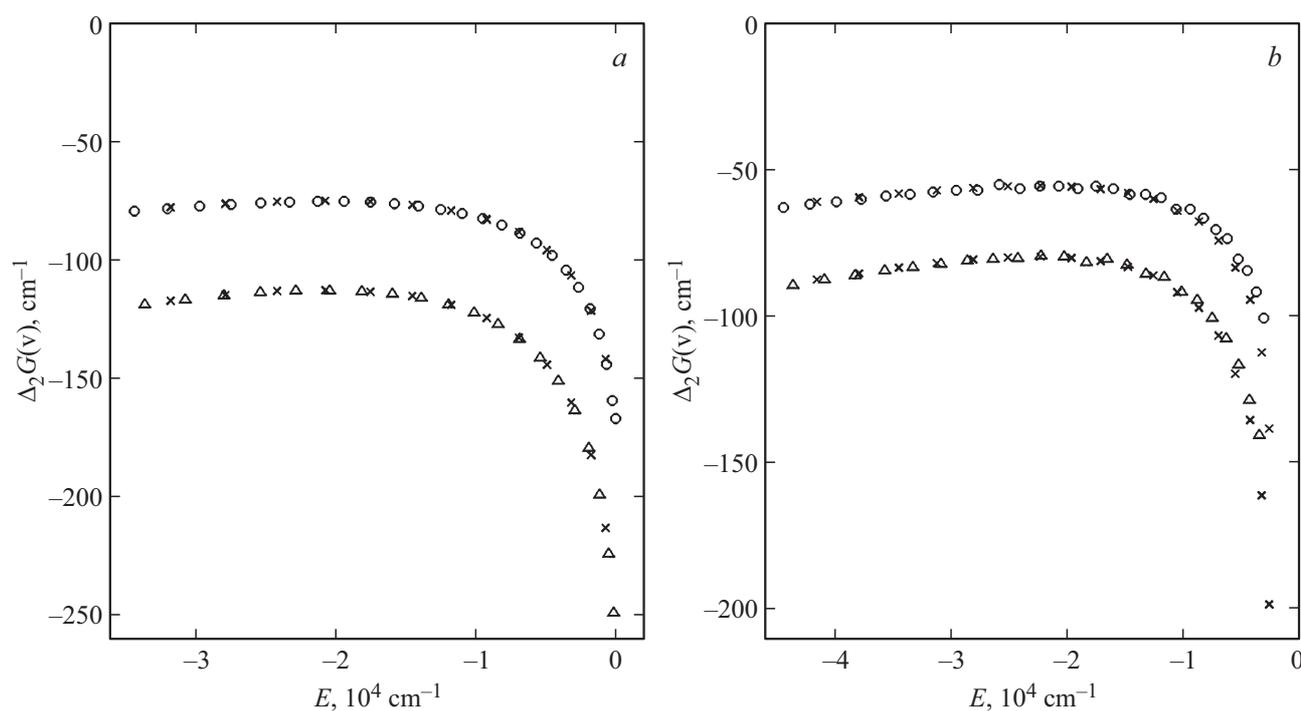
**Figure 4.** The second differences for isotopically substituted molecules are proportional to the reduced masses: (*a*) the second differences for $D_2$ and $T_2$ (as in Fig. 2) and superimposed second differences for $H_2$ (crosses) divided by the ratio of the reduced masses of deuterium and hydrogen ($M_{D2}/M_{H2} = 2$), and tritium and hydrogen ($M_{T2}/M_{H2} = 3$); (*b*) the second differences for DF and TF (as in Fig. 3) and the second differences for HF superimposed on them, divided by the ratio of the reduced masses of the DF and HF molecules ($M_{DF}/M_{HF} = 1.905$), and TF and HF ($M_{TF}/M_{HF} = 2.727$).

independence of the potential form from the reduced mass of the molecule. The hydrides are most useful in this regard because of the significant difference in the vibrational quanta of the three isotopes, hydrogen, deuterium, and tritium. The energy use as abscissa ensures the universality of the conditions for results comparison.

The availability of accurate data in the literature makes it possible to make such dependences for three isotopes of the hydrogen molecule ($H_2$, $D_2$, $T_2$) and hydrogen fluoride (HF, DF, TF), the data obtained are shown in Fig. 2 and 3. Fig. 2, *a* shows the dependence $F(v)$ on the energy scale $E = G(v) - D_e$. The values of depth of the potential energy well for all isotopic forms of hydrogen practically coincide in the adiabatic approximation, but the value of the harmonic frequency for them in this series decreases from $4401.21 \, cm^{-1}$ ($H_2$) to $3115.5 \, cm^{-1}$ ($D_2$) and $2546.4 \, cm^{-1}$ ($T_2$) [23], so the curves are at different heights. In these coordinates the value of the Herzberg anomaly (decrease in anharmonicity for the levels in the lower part of the potential energy well) decreases with increasing of the isotope mass. For three isotopes, we plotted the Morse term by the method described above, averaging $x^*$ value over the first seven levels for hydrogen and in the same energy range for two heavy isotopes. In Fig. 2, *a* the horizontal lines show the level at which the points of the Morse oscillator are located, the points themselves are not shown.

Fig. 2, *b* shows the energy dependence of the universal anharmonicity $x^*(E)$. The dependence on frequency disappeared, but the distance between the curves unexpectedly decreased slightly. Formally, this should mean that the anharmonicity decreases when the isotope mass increases. At that, at first thought, it seems that the shape of the curves did not change in the same way. This analysis requires a special study. The dimensionless universal anharmonicity $x^*$ in the main part of the potential energy well, where it still makes sense, takes values from 0.015 to 0.035, and varies for each isotope in interval approximately 0.015 units wide. The highest anharmonicity is observed for the hydrogen term $H_2$.

Literature data on the vibrational structure of the ground electronic state of HF, DF, TF molecules are processed according to the same scheme. The results are presented in Fig. 3, *a, b*. The picture is very similar to the hydrogen isotopes described above — a small Herzberg anomaly is noticeable on the second differences, which is reproduced in scale $x^*(E)$, but the intervals $x^*$ differ more strongly, and the mismatch of the curves is visible for different isotopes. It makes sense to carry out a detailed analysis of the practical possibilities of this approach after the accumulation of experimental data, including „abnormal" electronic adiabatic terms — they will show how sensitive the parameter $x^*$ is to the „features" of such terms.

As a conclusion, let's compare the second differences $F(v)$ vs. the isotope mass. It follows from (7) that they must be proportional to the reduced molecule masses (both factors in $v_e x^*$ depend on the root of the reduced masses). Fig. 4, $a$ shows the second differences for $D_2$ and $T_2$ (as in Fig. 2, circles and triangles) and the second differences for hydrogen superimposed on them, divided by the ratio of the reduced masses of deuterium and hydrogen (i.e. by 2), and tritium and hydrogen (i.e. by 3) (crosses). The same operation was carried out with the data for HF isotopes (Fig. 4, $b$). The agreement is excellent over the entire energy interval, so that the isotope effect does not introduce noticeable distortions into $x^*(E)$ dependence.

In particular, it becomes obvious that the second differences in the wavenumber scale look more natural than in the vibrational quantum number scale and are preferred in the analysis. This is especially important to keep in mind when considering „abnormal" electronic terms, in which the specific details of the arrangement of perturbed vibrational levels can be noticeably distorted.

## Conclusion

A comparison of the behavior of vibrational progressions for several molecules with an estimate of their parameters obtained using the Morse potential shows how accurately (or inaccurately) this potential describes the properties of diatomic molecules, for which experimental or calculated data are available in a wide frequency range. There are examples when, with a successful choice of the initial value of the anharmonicity parameter, it is possible to describe the vibrational structure with good accuracy. This means that for a number of molecules the arrangement of vibrational levels in the middle part of the electronic term and, less confidently, in its lower part satisfies the Morse conditions with practical acceptability. Deviations from constant anharmonicity in relative units practically coincide for isotopically substituted molecules, which confirms the physicality of the second differences $F(v)$ representation as a function of energy, but not vibrational quantum number. The dimensionless anharmonicity characteristic $x^*(v)$ makes it possible to compare, at least qualitatively, the degree of anharmonicity for different molecules. For example, for hydrogen $H_2$ the anharmonicity is more pronounced than for HF both on the average (averaged constant anharmonicity according to Morse) and in the amplitude of deviations from the average.

Note by G.S. Denisov. This topic occurs during our talk with M.O. Bulanin about 15 years ago, when we discussed the need that occurred for both of us to find for lectures to students the convincing examples of the practical application of the Morse function with an estimate of systematic errors, embedded by the founder. Separate fragments gradually accumulated, and this is what happened finally. In this aspect, the situation changed little since then, although we provide references mainly to publications of the current century. We are convinced that Mikhail Olegovich would appreciate the result. A detailed presentation of the first part of this material is accepted for publication in Spectr. Acta A. 2021.

## Conflict of interest

The authors declare that they have no conflict of interest.

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