



Absolute vibrational numbering from isotope shifts in fragmentary spectroscopic data

A. Pashov^{a,*}, P. Kowalczyk^b, W. Jastrzebski^c

^a Faculty of Physics, Sofia University, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria

^b Institute of Experimental Physics, Faculty of Physics, University of Warsaw, ul. Pasteura 5, 02-093 Warsaw, Poland

^c Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

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ABSTRACT

We discuss application of the isotope effect to establish the absolute vibrational numbering in electronic states of diatomic molecules. This is illustrated by examples of states with potential energy curves of both regular and irregular shape, with one or two potential minima. The minimum number of spectroscopic data (either term values or spectral line positions) necessary to provide a unique numbering is considered. We show that at favourable conditions just four term energies (or spectral lines) in one isotopologue and one term energy in the other suffice.

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1. Introduction

It is well established that absolute vibrational numbering can be determined from two sets of experimental term energies of the same electronic state in two isotopologues [1]. The main idea behind is that the electronic state in both molecules can be described with the same potential energy curve, i.e. both data sets have a common zero energy reference, usually denoted as T_e or Y_{00} . Let the rovibrational levels of the isotopologue with reduced mass μ_0 be expressed by a Dunham series

$$E_{vj} = \sum_{ij} Y_{ij} (v + 1/2)^i (J(J + 1))^j. \quad (1)$$

The absolute vibrational quantum number cannot be determined solely from the observed energy pattern of a single isotopologue since an expression similar to (1) can be found when v is substituted by $v + \Delta v$ while the term energies remain unchanged. A change in v will lead to a shift in the energy origin of the electronic state, Y_{00} , as well as change of other Dunham coefficients. The situation differs when levels of an isotopologue with reduced mass μ are also available. If small second-order effects [2] are neglected, these levels can be scaled as [1,3]

$$E_{vj}^{\text{iso}} = \sum_{ij} Y_{ij} \alpha^{i+2j} (v + 1/2)^i (J(J + 1))^j, \quad (2)$$

where the square root of the ratio of reduced masses is denoted as $\alpha = \sqrt{\mu_0/\mu}$. The common procedure at this point is to fit the experimental data relating to two isotopologues with the same set of Dunham coefficients. For the correct absolute vibrational numbering in both of them the root mean square error of the fit should be similar to the uncertainty of the experimental data. Alternatively, if the electronic state is represented directly by its potential energy curve (and not the Dunham expansion) the same potential is fitted to eigenenergies of both isotopologues. With the true vibrational numbering the potential should reproduce correctly energies of all the observed rovibrational levels.

It is a common belief among spectroscopists that for determination of vibrational numbering by the isotope effect the experimental data need to be sufficiently extensive to enable fitting a full set of Dunham coefficients or a potential curve for a given state. The goal of this paper is to point out and demonstrate that this is not a prerequisite for application of the isotope shift method. In the following sections we derive formulas which allow to determine the absolute vibrational numbering even from a very limited set of experimental levels and discuss possible uncertainties of this determination. Then we demonstrate usage of the method on few typical examples for problems encountered in spectroscopic research. One of them treats the case in which only high vibrational levels of an investigated state are observed. Here the extrapolation to the energy origin can be associated with large uncertainties and the method might be expected (incorrectly) to fail. We also analyse applicability of the method to electronic states with exotically shaped potential curves. In double-well potentials,

* Corresponding author.

E-mail address: pashov@phys.uni-sofia.bg (A. Pashov).

for example, the term energies cannot be described by a single Dunham series. Once again, many term energies may be experimentally inaccessible (e.g. levels from one of the two potential wells) and this may apparently cause the absolute vibrational numbering for the rest of the experimental data to be uncertain or arbitrary. However, we show that even in such cases it is possible to make use of the isotope effect.

2. Theory

Consider a smooth dependence of the energies of a diatomic molecule with reduced mass μ_0 on the vibrational and rotational quantum numbers $E_{vj} = F(x, y)$, where $x = (v + 0.5)$ and $y = J(J + 1)$ (for electronic states other than Σ states $y = J(J + 1) - \Lambda^2$ should be used instead). For the case of electronic states with regular potential energy curves this function may be the Dunham expansion, but other smooth functional forms are also possible. Here v does not necessarily equal to the true vibrational number. A similar functional dependence of the energy levels on x may be achieved by adding an arbitrary number to v , i.e. by shifting the function along the x axis. The same function $F(x, y)$ can then be used for another isotopologue of the molecule with reduced mass μ_i if the variables are scaled as [3]

$$x_i = \alpha(v + 0.5), \quad (3)$$

$$y_i = \alpha^2 J(J + 1), \quad (4)$$

where $\alpha = \sqrt{\mu_0/\mu_i}$. Therefore the change of the reduced mass can be treated as a change (usually small) of variables x and y ,

$$x_i = x + (\alpha - 1)(v + 0.5), \quad (5)$$

$$y_i = y + (\alpha^2 - 1)J(J + 1). \quad (6)$$

In regions where $F(x, y)$ varies slowly, one can use a Taylor series to approximate the energies of the isotopologue

$$E_{vj}^{\text{iso}} \approx F(x, y) + \frac{\partial F(x, y)}{\partial x} (\alpha - 1)(v + 0.5) + \frac{\partial F(x, y)}{\partial y} (\alpha^2 - 1)J(J + 1). \quad (7)$$

The energy shift $\Delta E_{vj} = E_{vj}^{\text{iso}} - E_{vj}$ of rovibrational level (v, J) due to the isotope effect is then

$$\Delta E_{vj} \approx \frac{\partial F(x, y)}{\partial x} (\alpha - 1)(v + 0.5) + \frac{\partial F(x, y)}{\partial y} (\alpha^2 - 1)J(J + 1). \quad (8)$$

One can see that the energy shift, which is an observable, depends explicitly on the absolute vibrational quantum number. This lifts the ambiguity in v since

$$v = \frac{\Delta E_{vj} - F_y(\alpha^2 - 1)J(J + 1)}{F_x(\alpha - 1)} - 0.5; \quad (9)$$

henceforth we use symbols $F_y = \frac{\partial F(x, y)}{\partial y}$ and $F_x = \frac{\partial F(x, y)}{\partial x}$. Given a pair of levels E_{vj}^{iso} and E_{vj} which are assumed to correspond to the same quantum numbers (the vibrational number does not need to be the correct one) the derivatives F_y and F_x are fixed because they are calculated for these values of x and y which correspond to E_{vj} . Actually the derivatives F_x and F_y are observables. For example F_x is associated with the change of the term energy between two successive vibrational levels and the absolute values of v are of no importance. By assuming the scaling of the x variable through the ratio of the reduced masses (3), however, the energy shift (8) becomes v dependent and allows the absolute value of v to be found. The derived expression may seem surprising since it tells us that the absolute vibrational numbering of the experimental term energies can be determined from the behaviour of $F(x, y)$ in a narrow interval of its arguments. It is important only to assure

that in this narrow interval the function F can be expanded sufficiently accurately in a Taylor series truncated after the first derivatives. The behaviour of the function outside this region is not important.

Our key point is that the determination of the true vibrational numbering may be based on experimental term energies even without assuming any particular functional form of the dependence E_{vj} . For example, consider an observed vibrational progression in the main isotopologue which leads to a series of term energies (E_{nj}, E_{nJ+2}) , where n is the relative vibrational label of the successive doublet. The derivatives may be approximated as

$$F_x \approx \frac{E_{n+1J} - E_{n-1J}}{2}, \quad (10)$$

$$F_y \approx \frac{E_{nJ+2} - E_{nJ}}{4J + 6}. \quad (11)$$

Since these formulas contain only energy differences, combinations of line frequencies may be used instead, e.g. in the presented case of three P and one R line of a given vibrational progression. Of course other combinations of experimental term energies are possible to evaluate F_x and F_y . Then, a single observation of term energy E_{nj}^{iso} in another isotopologue, which corresponds to the same pair of quantum numbers as in E_{nj} , allows the determination of the true vibrational quantum number from (9).

3. Uncertainty in v

Formula (9) allows us to set the lowest limit of an uncertainty σ_v of the absolute vibrational numbering. If the correspondence of $E_{v,J}$ and $E_{v,J}^{\text{iso}}$ to the same vibrational quantum number is certain, the main contribution to σ_v comes from ΔE_{vj} since both other terms contain small factors of $\alpha^2 - 1$ or $\alpha - 1$. Given an uncertainty of the experimental term energies δ , the uncertainty of the determined vibrational number would be

$$\sigma_v > \frac{\sqrt{2}\delta}{F_x(\alpha - 1)}; \quad (12)$$

here the uncertainties of F_x and F_y are neglected. For example, with typical values of $\alpha = 0.98$ and $F_x = 50 \text{ cm}^{-1}$ (F_x is of the order of the local vibrational spacing) an experimental uncertainty of 0.005 cm^{-1} would set the lowest limit of σ_v to 0.007, and when $\delta = 0.1 \text{ cm}^{-1}$, $\sigma_v > 0.14$, which is still much smaller than 1. The uncertainty σ_v increases as α approaches 1. Another critical case is that of levels close to the dissociation limit, where F_x is small. When $F_x = 6 \text{ cm}^{-1}$ and $\alpha = 0.99$, for example, $\sigma_v > 23.5\delta$ which exceeds 1 when $\delta = 0.05 \text{ cm}^{-1}$.

Formula (12) can be analysed also in a different way. With the $F(x, y)$ function fixed by the experimental data from the main isotopologue, let us predict the isotope shift. With the true vibrational number v_t the result will be given by Eq. (8), whereas with a vibrational number $v = v_t + 1$ the shift will differ by $F_x(\alpha - 1)$. Obviously when the experimental uncertainty is larger than $F_x(\alpha - 1)$, one cannot distinguish between the true and the wrong numbering. In the example considered in the previous paragraph, for $\alpha = 0.98$ and $F_x = 50 \text{ cm}^{-1}$, the uncertainty of the experimental isotope shift would have to be larger than 1 cm^{-1} in order to make a false assignment probable. But for $F_x = 6 \text{ cm}^{-1}$ and $\alpha = 0.99$, an uncertainty of 0.06 cm^{-1} would suffice to provide an ambiguous assignment.

There are particular values of α for which it might be possible to find several self-consistent vibrational numberings for a given set of experimental data. For example, let v_t denote the true vibrational quantum number corresponding to a pair of levels E_{vj} and

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