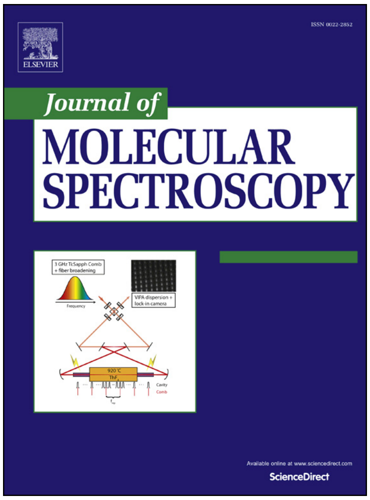

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Uncertainty of the potential curve minimum for diatomic molecules extrapolated from Dunham type coefficients

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In the traditional description of electronic states of diatomic molecules by means of molecular constants or Dunham coefficients, one of the important fitting parameters is the value of the zero point energy – the minimum of the potential curve or the energy of the lowest vibrational-rotational level – E_{00}. Their values are almost always the result of an extrapolation and it may be difficult to estimate their uncertainties, because they are connected not only with the uncertainty of the experimental data, but also with the distribution of experimentally observed energy levels and the particular realization of set of Dunham coefficients. This paper presents a comprehensive analysis based on Monte Carlo simulations, which aims to demonstrate the influence of all these factors on the uncertainty of the extrapolated minimum of the potential energy curve $U(R_e)$ and the value of E_{00}. The very good extrapolation properties of the Dunham coefficients are quantitatively confirmed and it is shown that for a proper estimate of the uncertainties, the ambiguity in the composition of the Dunham coefficients should be taken into account.

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I. INTRODUCTION

The first step in virtually every study involving diatomic molecules is to understand and describe their energy level structure. Usually the description is based on potential energy curves or molecular constants and, depending on the particular case, the electronic states can be treated separately, or as a group of coupled channels [1]. It is necessary to recall that both models describe the energy level positions, whereas experimental data usually consist of transition frequencies, i.e. they are proportional to differences between energy levels. Therefore it is important to find a reliable reference point from which the energy levels, of all electronic states of a molecule, are referenced. Traditionally in molecular spectroscopy this reference point is the minimum of the ground state potential curve: $U_{\mathrm{min}} = U(R_e)$ [2]. This choice is intuitive since it is mass-independent (i.e. common for all isotopologues within the Born-Oppenheimer approximation), and it sets the reference point at the lowest possible energy in the system. It has, however, serious drawbacks. On one hand, the reference point is connected to an unobservable quantity, moreover the potential curve itself is an approximation. On the other, within the description by molecular constants, there is no exact connection between the potential minimum and the position of any energy level.

There are better references, proposed and used in practice, but for some reason not widely accepted. One of them is the energy of the lowest rotational-vibrational level E_{vJ} at $v = 0$ and $J = 0$ (E_{00}) of the ground state. Although it is not always possible to observe transitions from/to this level, its energy is an observable quantity and provides a reference point which is free from extrapolation errors. In cases when this level has not been observed experimentally and its energy needs to be extrapolated from the molecular constants, it is believed that this extrapolation leads to a smaller uncertainty in E_{00} than in the case of U_{min}. The lowest vibrational level $v'' = 0$ in the ground states is usually always observed, but in the excited states due to unfavourable Frank-Condon factors the spectroscopic observations may start from $v'' = 1$ or even higher vibrational levels. In such cases the extrapolation towards E_{00} and U_{min} is more uncertain.

Another possibility is to take the energy of the atomic asymptote of the ground state as an energy reference. It became possible since the conduction of the first photoassociation experiments [3], where transition frequencies from continuum states lying very close (several MHz) to the atomic asymptote have been measured. Although it is a good reference, it is not always applicable, due to the fact that until now photoassociation spectroscopy has been realized in a very limited set of atomic species. Moreover, often the photoassociation covers a limited set of energy levels and even when the positions of the last few energy levels are known from the atomic asymptote, they are not connected with transitions to the low lying levels of the electronic state. In such cases the reference energy remains isolated.

In order to understand the importance of reliable reference energy for every molecule, it is sufficient to recall that the energies of all excited state levels are determined using this reference. If, for example, a new improved description of the ground state is reported, it is necessary to recalculate all the energies on the excited states reported so far. Another important issue, related to the choice of energy reference, is the determination of the dissociation energy of an electronic state - D_e. Usually the dissociation energy is defined as the difference between the minimum of the potential curve U_{min} for this state and