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Impact of the dipole-moment representation on the intensity of high overtones

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ABSTRACT

Calculating intensities of ro-vibrational transitions is particularly challenging for transitions from a given vibrational state to all upper states up to the dissociation limit because their probabilities decrease exponentially with increasing Δn, the change in the vibrational quantum number. The experimental intensities available for low-Δn values are well reproduced by a variety of models but the models can greatly diverge in predicting the intensities of unobserved high-overtone transitions, the divergence rapidly increasing with the overtone number. In this paper, we investigate the impact of the dipole-moment function (DMF) representation on the high-overtone intensity simulation of the CO molecule. We tested various DMF forms including pointwise representation combined with cubic-spline interpolation, power and trigonometric expansions, and Padé approximants. Numerical calculations were performed with the highly accurate empirical potential-energy function (PEF) of Coxon and Hajigeorgiou (2004) using quadruple-precision arithmetic. Most calculated intensities fall off in the entire range of transitions according to the Normal Intensity Distribution Law (NIDL) (Medvedev, 2012). The slope of the NIDL trend line varies little between different analytical DMFs for a given PEF since the slope is basically associated with the PEF. Based on the NIDL, the limits within which the simulated intensities fall off up to the dissociation limit can be established. We claim that DMFs represented by analytical functions yield best results for all transitions. The pointwise functions (interpolated, in particular, by the conventional cubic splines) result in an unphysical flattening of the intensities at high-Δn transitions, $\Delta n > 7$ for CO.

1. Introduction

Contemporary spectroscopic databases contain both measured and calculated line parameters. In recent years, the importance of weak lines, such as high-overtone vibrational transitions, which are more challenging to measure, has been recognized, and the calculated data has become prevalent. Moreover, calculations often extend to transitions up to the dissociation limit, which poses a question about the validity of the existing tools for performing such calculations. Recently, we have found [1] (**Li15**) that matrix elements of the dipole moment for $0 \rightarrow n$ transitions, d_{0n}, in carbon monoxide were incorrectly calculated for $n > 11$ using Le Roy's LEVEL code [2], originally intended and successfully used for transitions between low-lying vibrational levels. In particular, the calculated intensities showed unphysical flattening (saturation) at high values of Δn (difference between vibrational levels; note that here we chose to use "Δn" instead of conventional "Δv" to reflect that the lower state is always the ground vibrational state although we believe the discussion could be extended to overtone hot bands as well). Therefore, the transitions with $\Delta n > 11$ were excluded from the published CO line list [1]. Further inspection revealed that the flattening also occurred for other molecules at different Δn values when the intensities were calculated using double-precision arithmetic. We investigated this point in more detail and found that, for a given potential-energy and dipole-moment functions (PEF and DMF), the intensities with the physically justified falloff up to the dissociation limit could be obtained using quadruple-precision arithmetic [3].

In this paper, we address some other issues concerning intensity predictions for high-Δn transitions. Specifically, we ask the question: how do the calculated transition moments depend on various forms, empirical or *ab initio*, of DMF for a given PEF, as well as on the interpolation or modeling methods used with the *ab initio* DMF data? Recently, Li et al. [1,4] found that the intensities were extremely sensitive to the DMF used in the calculations.

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In Figs. 1, 3, 5 and 7 of Ref. [4], seemingly identical DMFs produced intensity values differing by up to 400%! It was also determined in **Li15** that, for $\Delta n > 4$, the *ab initio* DMF must be calculated at a much finer grid than in any of the previous attempts. At $\Delta n > 5$, the intensities became very sensitive to the interpolation or modeling method used to calculate the DMF between the points of the grid. Here, we demonstrate, in particular, that the conventional interpolation with cubic splines applied to the *ab initio* DMF data [1,5] fails for high overtone transitions. Further, we show that the Normal Intensity Distribution Law (NIDL) can be used to predict the intensities of unobserved transitions with uncertainties that can be estimated. Thus, while it is impossible, in principle, to establish the best DMF form to represent the true molecular dipole, it is nevertheless possible to indicate the upper and lower limits of the estimated intensities. The latter task, however, can be completed only after a similar investigation of PEF is performed. While our previous experience testifies that the PEF has little effect at low-Δn transitions in diatomics, the applicability of empirical PEFs to calculations of very high-Δn transitions is not obvious because of their incorrect asymptotic behavior in the united-atom limit.

2. Numerical experiments

We solve the radial Schrödinger equation in its simplest form, without any J- or mass-dependent terms, see Eq. (4) of Coxon and Hajigeorgiou [6],

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} + U(R) - \varepsilon_n\right]\psi_n(R) = 0, \tag{1}$$

where the reduced mass M and the PEF $U(R)$ are for the CO molecule. The PEF is given in Ref. [6] by Eq. (9) with the parameters from the last column of Table II, the PEF parameters being taken with all digits including those subscripted. The DMF is basically taken in two forms, empirical and *ab initio*, derived for CO in **Li15**.

The CO empirical DMF is a sixth-order polynomial with coefficients from Table 4 of **Li15**. We will also call it the "full-empirical DMF" because a truncated, "linear-empirical DMF" playing a special role in our analysis will be used as well.

The CO *ab initio* DMF is tabulated in the interval of 1.5–4 bohr with varying step of 0.02–0.05 bohr, see Table S3 in **Li15**. For the purpose of numerical integration, it is fit using both analytical models and non-analytical interpolating functions. Five analytical functions are used: a tenth-order Taylor series, a trigonometric expansion, and three Padé approximants. As non-analytical functions, we use conventional [7] cubic splines with so-called "natural" boundary conditions as well as a hybrid cubic spline (**Li15**) that combines the empirical DMF between the turning points of the sixth level with the *ab initio* DMF outside.

The full-empirical and *ab initio* DMFs along with their difference are shown in Fig. 1. The difference is a smooth curve except for four points at smallest R. This was the reason to use, besides the original set of the *ab initio* DMF points, a corrected set, in which those four points were replaced with their empirical counterparts in order to test how this seemingly small change will affect the calculated intensities. Note that the above difference is of the same order of magnitude as the one between two *ab initio* DMFs of **Li15** obtained by two different methods (see Fig. 3 in **Li15**). Thus, the effect of the difference between two *ab initio* DMFs on the calculated intensities will mimic the common effect of changing the *ab initio* method to calculate the DMF points.

The polynomial expansions for two empirical DMFs are written in the form

$$d(R) = \sum_{i=0}^{6} M_i[(R - R_e)/R_e]^i, \tag{2}$$

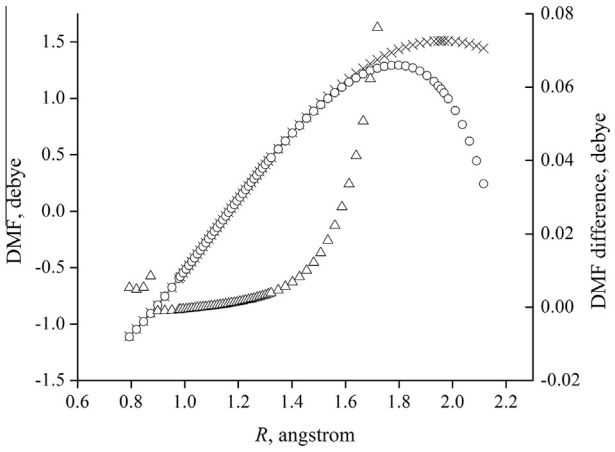

Fig. 1. The *ab initio* (crosses) and empirical (circles) dipole-moment functions (left ordinate) and their difference, the first minus the second (triangles, right ordinate).

where equilibrium bond length $R_e = 2.13222$ bohr and parameters M_i are taken from **Li15**. In the full-empirical DMF, all terms of the sum in Eq. (2) are retained whereas, in the linear-empirical one, terms i = 2–6 are omitted.

The polynomial expansion for modeling the *ab initio* DMF of **Li15** is

$$d(R) = \sum_{i=0}^{10} a_i[(R - R_0)/R_0]^i, \tag{3}$$

where $R_0 = 2$ bohr is fixed and a_i are adjustable parameters. Here and below, the parameters are found by least-squares fitting. The trigonometric expansion for the *ab initio* DMF of **Li15** is written in the form

$$d(R) = d_0 + \sum_{i=1}^{4}\{s_i \sin[i(R - R_0)/w] + c_i \cos[i(R - R_0)/w]\}, \tag{4}$$

where $R_0 = 2$ bohr is fixed and d_0, w, s_i, c_i are adjustable parameters. The first Padé approximant (denoted Padé 1) to fit the *ab initio* DMF of **Li15** is written as

$$d(R) = \frac{Az^3 + Bz^4 + Cz^5 + Dz^6}{\prod_{i=1}^{5}\left[\left(z - \frac{b_i}{w}\right)^2 + a_i^2\right]}, \quad z = \frac{R}{w}, \tag{5}$$

where a_i, b_i, and A, B, C, D, w are adjustable parameters. The second Padé form to be used (Padé 2) is

$$d(R) = \frac{z^3}{1 + z^7}\sum_{i=0}^{4} a_i T_i\left(\frac{z-1}{z+1}\right), \quad z = \frac{R}{R_c}, \tag{6}$$

where $T_i(x)$ are Chebyshev polynomials, $R_c = 2.13$ (Padé 2 v0) or 3.7 (Padé 2 v1) bohr is fixed, and a_i are adjustable parameters. Equations (5) and (6) satisfy the conditions that the limiting behavior were $c_{+3}R^3$ at $R \to 0$ and $c_{-4}R^{-4}$ at $R \to \infty$, as proposed by Goodisman [8], and the polynomial in the denominator had no zeros at the real positive half-axis, as did the Padé forms in Refs. [9,10]. In principle, the asymptotic parameters could be fixed at known atomic-based values of $c_{+3} = 58.6$ a.u. and $c_{-4} = 0.134\text{D} \times \text{Å}^4$ [11,12], but this goes beyond the scope of the present paper.

Two additional Padé forms of DMF, Padé 2 v2 and Padé 3, are based on different sets of data. The former, given by Eq. (6) with $R_c = 3.7$ bohr, is based on the *ab initio* data due to Langhoff and Bauschlichter [13] (**Langhoff95**) calculated at a coarser grid than in **Li15**. Padé 3 is the one proposed by Chackerian and Tipping [9]. The fitted parameters in Eqs. (3)–(6) for the original and