

## Comment on the paper “Further contributions to the energy levels of a perturbed anharmonic oscillator: Application to adiabatic corrections”

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# Comment on the paper "Further contributions to the energy levels of a perturbed anharmonic oscillator: Application to adiabatic corrections"

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Hadlinger *et al.* have recently claimed<sup>1</sup> to derive values of five coefficients  $\chi_i$  for  $^1\text{H}^{35}\text{Cl}$  and five more  $\chi_i$  for  $^2\text{H}^{35}\text{Cl}$  from the values of the parameters  $U'_{kl}$ , or the equivalent  $\Delta_{kl}^{\text{H,Cl}}$ , determined from the spectral analysis by Coxon and Ogilvie.<sup>2</sup> In a previously published paper,<sup>3</sup> some values equivalent in principle to their  $\chi_i$  but designated  $h_j$  were determined. However, no value of  $h_5^{\text{H}}$  could be determined<sup>3</sup> in that work because it was demonstrated<sup>3</sup> that the remaining value  $\Delta_{0,2}^{\text{H}}$  could provide not additional information but merely a consistency test for  $h_2^{\text{H}}$ . A value of  $\chi_5$  or our  $h_5^{\text{H}}$  can be derived from only  $\Delta_{2,1}^{\text{H}}$ ,  $\Delta_{1,3}^{\text{H}}$  or  $\Delta_{0,5}^{\text{H}}$ , or the equivalent intermediate quantities  $U'_{2,1}$ ,  $U'_{1,3}$  or  $U'_{0,5}$ , but no such value was determined in the analysis, and accordingly none was

reported.<sup>2</sup> Therefore both values of  $\chi_5$  must be regarded as spurious.

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<sup>1</sup>G. Hadlinger, Y. S. Tergiman, and G. Hadlinger, *J. Chem. Phys.* **88**, 4351 (1988).

<sup>2</sup>J. A. Coxon and J. F. Ogilvie, *J. Chem. Soc. Faraday Trans. II* **78**, 1345 (1982); minor typographical errors occur that are here corrected: in Table 3,  $U_{3,0} = 19.1910$ , and on page 1361  $k_e = 516.332\,15\,\text{N m}^{-1}$  and  $a_0 = 2.111\,393 \times 10^7\,\text{m}^{-1}$ .

<sup>3</sup>J. F. Ogilvie, *Chem. Phys. Lett.* **140**, 506 (1987).

## Reply to the Comment on the paper "Further contributions to the energy levels of a perturbed anharmonic oscillator: Application to adiabatic corrections"

G. Hadlinger and Y. S. Tergiman

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Concerning Ogilvie's comment on the calculation of  $\chi_5$ , it seems necessary to explain in detail our process. In page 4355 (Subsection III.B) of Ref. 1, it is said that the  $\chi_i^{^1\text{H}^{35}\text{Cl}}$  and  $\chi_i^{^2\text{H}^{35}\text{Cl}}$  expansion coefficients of the adiabatic corrections  $\Delta_{AB}^{\text{ad}}(R)$  are calculated by use of "the methods described in Ref. 2." Indeed, for determining these coefficients, we have used relation (10) of Ref. 2:

$$\chi_i^{\text{AB}} = k_i - (B_e b^2)^{\text{BO}} h_i^{\text{BO}}$$

which involves the  $k_i$  expansion coefficients of the effective potential  $U(R)$  and the  $h_i^{\text{BO}}$  expansion coefficients of the Born–Oppenheimer potential. Having at our disposal the values of  $U_{01}(^1\text{H}^{35}\text{Cl})$ ,  $U_{01}(^2\text{H}^{35}\text{Cl})$ ,  $U_{10}(^1\text{H}^{35}\text{Cl})$ ,  $U_{10}(^2\text{H}^{35}\text{Cl})$ ,  $U_{11}(^1\text{H}^{35}\text{Cl})$ ,  $U_{11}(^2\text{H}^{35}\text{Cl})$ ,  $U_{20}(^1\text{H}^{35}\text{Cl})$ ,  $U_{20}(^2\text{H}^{35}\text{Cl})$ , and  $U_{21}(^1\text{H}^{35}\text{Cl}) = U_{21}(^2\text{H}^{35}\text{Cl})$  together with corresponding Born–Oppenheimer values—from Table 2 of Ref. 3—it has been possible to obtain estimates for the  $k_i$  coefficients up to  $i = 5$  and for the  $h_i^{\text{BO}}$ . Although the uncertainty in the relation  $U_{21}(^1\text{H}^{35}\text{Cl}) = U_{21}(^2\text{H}^{35}\text{Cl})$  is

unknown, our calculations are based on the assumption that this equation is valid. This assumption was also made in the original fit of the data by Coxon and Ogilvie. Then the  $\chi_i^{^1\text{H}^{35}\text{Cl}}$  and  $\chi_i^{^2\text{H}^{35}\text{Cl}}$  have been determined. From the knowledge of  $\Delta_{01}^{\text{H}}$ ,  $\Delta_{10}^{\text{H}}$ , and  $\Delta_{11}^{\text{H}}$  (fit B of Table 2 of Ref. 3), the values of  $\chi_i^{\text{H}}$  for  $i \leq 3$  have been obtained from Eq. (23) of Ref. 2 and results of Ref. 4. Alternatively, we have also calculated the values of  $\chi_i^{\text{H}}$  for  $i \leq 3$  by use of Eq. (27) of Ref. 2. The results are in very good accordance. For the calculation of the  $\chi_i^{\text{Cl}}$ , we have used formula (28) of Ref. 2. All these results are given in Table II of Ref. 1 (in  $\text{cm}^{-1}$ ).

<sup>1</sup>G. Hadlinger, Y. S. Tergiman, and G. Hadlinger, *J. Chem. Phys.* **88**, 4351 (1988). There is a minor misprint. In paragraph B, line no. 8, replace Table II (fit B) by Table II (fit A and fit B).

<sup>2</sup>G. Hadlinger and Y. S. Tergiman, *J. Chem. Phys.* **85**, 6853 (1986).

<sup>3</sup>J. A. Coxon and J. F. Ogilvie, *J. Chem. Faraday Trans. II* **78**, 1345 (1982).

<sup>4</sup>N. Bessis, G. Hadlinger, and Y. S. Tergiman, *J. Mol. Spectrosc.* **107**, 343 (1984).