

The importance of kinetic energy coupling in the vibrational spectra of small cluster dimers

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INTRODUCTION

The Watson molecular Hamiltonian in normal coordinates for a non-rotating top is:

$$H = \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - \frac{1}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} + V(Q_1, Q_2, \dots) - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha}$$

where $\hat{\pi}_\kappa$ is the vibrational angular momentum in normal coordinates. The $\mu_{\alpha\beta}$ tensor can be expanded into a power series and that for most cases the series can be truncated after the first term. [1] The mode coupling in the kinetic energy operator is usually neglected by many authors. This simplifies considerably the Watson Hamiltonian and it is also justified by the fact that the coupling is usually weak, being considered irrelevant for heavy molecules. Calculations performed by several authors [1,2] showed that the contributions of the kinetic energy couplings (also termed Coriolis coupling) to the fundamental frequencies may be of the order of tens of cm^{-1} . Hence for high level spectroscopy studies the inclusion of the full Watson Hamiltonian components is mandatory. In this work we use the VSCF formalism to investigate the importance of Coriolis coupling in the vibrational spectra of small dimers as $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O}_2)_2$ and $(\text{NH}_3)_2$. Our aim is to show how far the vibrational analysis may be taken without considering the coupling of normal modes in the kinetic energy operator.

METHODS

The electronic structure calculations were done with the GAMESS package at the MP2/aug-cc-pVTZ level of theory. Our VSCF code is an extended version of the GAMESS implementation that enables calculations including the Coriolis coupling discussed above. The potential energy operator used is based in the QFF representation. [3]

RESULTS AND DISCUSSION

The average and the maximum Coriolis contribution for each dimer are shown in table 1.

Table 1: Average and Maximum Coriolis contribution (in cm^{-1}) to the fundamental transitions of $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O}_2)_2$ and $(\text{NH}_3)_2$.

| | Avg | Max |
|----------------------------|-------|--------|
| $(\text{H}_2\text{O})_2$ | 23,55 | 72,81 |
| $(\text{H}_2\text{O}_2)_2$ | 1,28 | 4,97 |
| $(\text{NH}_3)_2$ | 19,46 | 108,78 |

Coriolis may play an important role as it can cause a shift in frequencies as large as 100 cm^{-1} , although they usually do not exceed 50 cm^{-1} . For hydrogen peroxide dimer, the error in not including is negligible for most purposes, except for the lowest bending mode ν_{18} . The reason is the small rotational constants for this cluster. For ammonia and water dimer, the rotational constants are considerably larger. Hence the impact of Coriolis coupling is more pronounced.

CONCLUSIONS

In this work we investigated the importance of the vibrational mode coupling in the kinetic energy operator for three cluster dimers: $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O}_2)_2$ and $(\text{NH}_3)_2$. It was found that there can be considerably shifting in the fundamental transition frequencies, especially when the rotational constants are not very low. This coupling may be important not only for high level spectroscopy but also to correctly probe potential energy surfaces.

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