Vibrational and Rotational Contributions to Molecular Properties.

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Errata

1. Page 16, Equation (2.23). The missing definition of H_{21} is

$$\lambda H_{21} = -2\sum_{k,l}\left(\frac{\omega_l}{\omega_k}\right)^{\frac{1}{2}} q_k p_l \sum_{\alpha} B_\alpha \zeta_{kl}^{\alpha} J_\alpha$$

2. Page 130, Reference [11]. Elliot should be spelt Elliott.

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

[redacted]

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Abstract

This thesis presents an investigation of vibrational and rotational contributions to molecular properties. The theory for ground and excited rotational-vibrational state properties, pure vibrational polarizabilities, the effect of deuterium isotopic substitution and thermal corrections to molecular properties is outlined and applied to a series of eleven small molecules. Studied molecules include the second-row hydrides (SiH_4, PH_3, H_2S, HCl), the fluoromethanes (CF_4, CHF_3, CH_2F_2, CH_3F), acetylene (C_2H_2), ethene (C_2H_4) and ethane (C_2H_6). Although electrical properties such as dipole and quadrupole moments, mean polarizabilities and polarizability anisotropies have been studied, the theoretical methods described are entirely general and able to be extended to other molecular properties. Two methods for calculation of electrical property derivatives have been utilised; a least-squares approach has been used for the majority of work in the present thesis while a central-difference method was utilised for work on ethane. Vibrational corrections have been combined with highly accurate BD(T) electrical properties to provide high-quality vibrationally averaged estimates. Extensive comparision of theory with experiment has been performed for the studied molecules and where experiment and theory disagree, a concerted attempt has been made to resolve any discrepancies.

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