ADDITIONS AND CORRECTIONS

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Y. Wang, J. Tremmel, J. De Smedt, C. Van Alsenoy, H. J. Geise,* and B. Van der Veken: Ab Initio Determination of the Force Field of Dichloromethane, Verified by Gas-Phase Infrared Frequencies and Intensities and Applied to a Combined Electron Diffraction and Microwave Investigation of Geometry

Page 5919. Recently we published[1] an ab initio determined force field of CH_2Cl_2 and verified it by gas-phase IR frequencies and intensities and applied it in a combined electron diffraction and microwave investigation of geometry.

Unfortunately, no reference was made to previous work by Duncan and co-workers, who in an elegant and extensive study[2−6] determined two complete force fields: one empirically determined general harmonic force field[4], and another based on ab initio calculations at the HF-SCF/6-31G** level.[6]

The assignment of the IR fundamental modes in the rotovibrationally complex gas-phase spectrum by Duncan et al.[2] (henceforth abbreviated as DEA) was supported by an extensive investigation and assignment of rotational transitions.[2,3] Wang et al. (henceforth abbreviated as WTD) suppressed the rotational fine structure by pressure broadening. Their assignment was supported by the comparison of experimental IR band intensities with calculated ones. Both assignments agree to within 1 cm^{-1} and corroborate Saëki and Tanabe's conclusion[7] that the weak band at 1430 cm^{-1} is the CH_2 scissoring mode and the strong band centered at 1467 cm^{-1} is a combination band.

The DEA force field was calculated at the 6-31G** level and the WTD force field at the 6-31G**/66-31G* level. The difference is in the way of scaling. Duncan et al. chose for an intuitive division of the symmetry coordinates in four groups (i.e., four scale factors). Wang et al. after a statistical analysis of various possibilities arrived at a division in three groups (i.e., three scale factors). Numerical values of the force constants of the two scaled, theoretical fields differ up to 10%. Root-mean-square deviations of calculated frequencies with experimental ones amount to 6.6[6] and 9.6 cm^{-1},[1] respectively. However, the difference in the degrees of freedom (4 vs 3) is at the root of the difference in rms values. On statistical grounds[8] both fields are equal. Duncan et al. noted four serious discrepancies between the DEA empirical and the DEA calculated force constants. The authors considered[6] the calculated values more reliable than the empirical ones. Interestingly, in the WTD force field three of these four discrepant force constants have values in between those of the two DEA fields.

Simple valence arguments rationalize[1] all signs and almost all relative magnitudes of the calculated interaction constants, which supports the reliability of the fields.

References and Notes

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