

Plane Fundamental Modes of Vibration of Deuteroethylenes

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LETTERS TO THE EDITOR

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Plane Fundamental Modes of Vibration of Deuteroethylenes

In the first part of a recent paper, Wu¹ has discussed the "assignment" of the plane vibration frequencies of the three isomeric deuteroethylenes, which had been calculated by Verleysen and the writer.² By the "assignment" of a vibration of the isomer, Wu evidently means its correlation to the "corresponding vibration of C₂H₄," the same notation being used for both. Whether such a correlation should always be possible without ambiguity is not examined. The general conclusion reached is that the groups CH₂, CHD, CD₂ markedly preserve their individuality in the vibrations of the CH₄ and CH₃D₂ molecules; this is just why an assignment of the vibrations is possible. The conclusion agrees entirely with previous work on C₂H₄.³

It is the purpose of this letter to call attention to papers⁴ in which the same results had already been obtained on a completely quantitative basis. A numerical quadratic potential function was computed from the experimental data obtained by Bonner⁵ for C₂H₄, giving a quantitative statement for the coupling of the two separate groups in the molecule through the double bond C=C. The potential function was used to compute the vibration frequency spectrum of monodeuteroethylene, agreeing with the experimental values within less than 1.5 percent.^{6, 7} Less satisfactory agreement was obtained in the case of diisomers and of C₂D₄,⁸ the largest discrepancy, in a single case, however, being as high as 5.5 percent. The reason for it is to be found in the inherent indeterminacy which remains in the choice of the potential function, if it is determined only by the data from C₂H₄. The new additional experimental data will enable us to remove the indeterminacy and to compute a potential function for all the ethylenes, the accuracy being finally limited by the unknown anharmonicities of the vibrations.

For C₂H₃D, the three C₂H₂D₂ and C₂D₄, besides the frequency spectrum, all the plane modes of vibration have been calculated. The drawings visualize well the extent to which the modes of vibration can be considered as internal fundamental vibrations of two nearly independent groups CH₂, CDH or CD₂ in the molecule (eventually coupled with a CC vibration), or, for the lowest frequencies, as rotations of these rigid groups. (A special notation for this kind of vibrations is desirable). There are cases, especially

for C₂H₃D, where the notation used by Wu seems to call for a modification.

There is another general way of interpreting the results, that discloses a close connection between the frequency spectrum and the corresponding modes of vibration: the nearer a frequency of C₂H₃D or C₂H₂D₂ lies to a frequency of the completely symmetric molecule C₂H₄ or C₂D₄, the more the corresponding mode of vibration resembles the neighboring mode of C₂H₄ or C₂D₄. If the frequency considered lies near two or more frequencies of C₂H₄ or C₂D₄, the corresponding mode of vibration appears as a combination of the neighboring modes of the completely symmetrical molecule. In the application of this rule, only those neighboring modes of C₂H₄ and C₂D₄ are to be considered that possess the symmetry of the mode investigated.

For instance, in the case of C₂H₃D, to the frequency 1579 cm⁻¹, which lies quite near to the isolated frequency 1623 cm⁻¹ of C₂H₄ and the similar frequency of C₂D₄, corresponds a mode of vibration which looks highly symmetrical, although the molecule itself is entirely dissymmetrical. In fact, in the total energy of the vibration as much as 91.5 percent is due to component motions that keep the full symmetry of the C₂H₄ molecule. On the other hand, to the 2266 cm⁻¹ frequency of the same molecule corresponds a mode which is a mixture in practically equal proportions of the four modes of different symmetry possessed by C₂D₄ in the neighborhood of that frequency.

From a knowledge of the modes of vibration qualitative predictions, which have already proved useful, can be drawn for the intensities and polarizations in the Raman and the infrared spectrum. Fuller discussion, examples and graphical illustrations will be found in the quoted papers.^{3, 7}

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