Structural Deductions from the Vibronic Spectra of Ethene and Ethene-d₄

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 $\Delta m = 1$ nuclear transitions induced by second-order effects. These effects are found to play an important role near the g-minimum directions.

¹ A. Zalkin, H. Ruben, and D. H. Templeton, Acta Cryst. 15, 1219 (1962). ³ K. S. Krishnan, Phil. Trans. Roy. Soc. London A237, 135 (1939). ³ J. A. Cowen and G. T. Johnston, J. Chem. Phys. 44, 2217 (1966).

Comments

Structural Deductions from the Vibronic Spectra of Ethene and Ethene- d_4

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In a recent article on the vibronic absorption spectra of ethene and ethene-d4, McDiarmid and Charney¹ identified two vibrational progressions for C₂H₄ and three for C₂D₄ between 46 000 and 57 000 cm⁻¹. From the magnitude of the ratio of the "primary" vibrational intervals of C_2H_4 and of C_2D_4 , the progressions were deduced to be of a torsional vibration. It was stated that the ratio was very different from the value of 0.93 predicted for a mode involving the entire methylene group. The purpose of these remarks is to indicate that an alternative bending vibration might be involved, and further that a previously unexplained interval of 150 cm⁻¹ might be solved on that basis. A consequence of the postulated alternative vibration scheme is that new evidence for the structure of the electronically excited state may be derived. In view of the importance of ethene as the simplest stable π -electron hydrocarbon, all clues to the geometric structure of its excited states are valuable with reference to valence theory.

The average vibrational intervals of the primary progressions can be computed² to be 797 ± 45 cm⁻¹ for C_2H_4 and 547 ± 19 cm⁻¹ for C_2D_4 , with secondary or "hot" progressions of interval 792 ± 39 , and 546 ± 29 , and 547 ± 19 cm⁻¹, respectively. The ratio (and standard deviation) of the frequencies of the primary progressions is 0.687 ± 0.045 . However if all the data for the several progressions are used (unweighted), the average frequencies are 795 ± 59 cm⁻¹ for C₂H₄ and 547 ± 40 for C₂D₄; the resultant ratio is $0.688 \pm$ 0.071. The magnitude of the frequencies, as well as the effects of isotopic substitution, indicates that bending rather than stretching modes are involved, and further the magnitude of the ratio indicates by its proximity to 0.7 that only slight motion of the carbon atoms is involved. At least two vibrational modes of planar (D_{2h}) ethene fit these criteria, the $\nu_4(a_u)$ torsional mode as previously assigned, and the out-of-plane bending mode $\nu_7(b_{1u})$ for which the theoretical isotope

ratio³ for C_2H_4 and C_2D_4 is 0.756. This ratio is within a reasonable distance of the measured ratio of 0.688, particularly if the larger standard deviation of 0.071 is accepted as being applicable. (The experimental ratio³ of ν_7 for the ground state of C_2H_4 and C_2D_4 is in fact precisely the calculated value 0.756).

If the ethene molecule were to distort from coplanarity of the equilibrium nuclear positions in the manner described by one extreme of the amplitudes of the atomic displacements in the ν_7 mode of planar ethene, the effect in the electronically excited state would be to diminish the repulsion due to the new occupancy of the π^* antibonding orbital.⁴ The shape of the molecule, in the event of a large distortion, would then resemble that of an eclipsed ethane molecule from which two (eclipsing) hydrogen atoms had been removed. Thereby the axes of the two methylene groups would be neither collinear nor parallel. In such a molecule, the vibration corresponding to the v_7 mode of ethene is totally symmetric (a_1) under the species C_{2v} . As four other internal vibrations are also totally symmetric, it is not possible to calculate the isotope effect on the bending vibration of interest without some assumptions about both the internuclear separations and the frequencies of the other modes. However it is likely that the frequency ratio would be between 0.7 and 0.8, because only slight carbon motion occurs during the vibration. As the bending vibration being considered is totally symmetric under C_{2v} , the selection rules allow that vibration to be excited as a result of the electronic transition. Thus the nonplanar C_{2v} structure has the qualities both of being a physically reasonable shape under the conditions of the $\pi^* \leftarrow \pi$ transition forming the excited state, and of being attainable under the selection rules in a vibration of approximately the observed frequency ratio.

Furthermore the estimates of the ground-state vibrations giving rise to the hot bands, 1077 ± 79 cm⁻¹ and 747 ± 45 cm⁻¹, while particularly the former is relatively large, are not impossibly distant from the ν_7 fundamental frequencies of 949 and 720 cm⁻¹ for C₂H₄ and C₂D₄, respectively. It is to be noted that the previous estimates¹ of the ground-state frequencies, 1089 ± 60 cm⁻¹ (an inaccuracy of Ref. 1 is here corrected) for C₂H₄ and 746\pm21 cm⁻¹ for C₂D₄, were also markedly greater than the accepted values¹ for the torsional vibration, 1025 and 726 cm⁻¹, respectively.

Finally, the assignment, proposed above, of the mode involved in the observed progressions leaves free the torsional mode for other purposes, for instance, the "unexplained physical phenomenon" of Ref. 1. The vibrational frequency of 149 ± 15 cm⁻¹ observed in the vibronic spectrum of $C_2D_4^1$ is of a magnitude suitable for the torsional mode of the deuterated molecule, by comparison with hydrazine- d_4 , for which this frequency is 300 cm^{-1,5} and with ethane and ethane- d_6 , for which this mode has the frequencies 275 and 200 cm⁻¹, respectively.³ The appearance in the C_2D_4 spectrum of the torsional vibration, which is not totally symmetric under C_{2v} , can be taken as an indication that the excited state may not be exactly in the eclipsed form, but rather slightly staggered.

In conclusion, the essence of the preceding analysis is that the vibrational structure of the electronic absorption spectra of C_2H_4 and C_2D_4 may be more readily consistent with an almost eclipsed, nonplanar structure for the first excited-singlet electronic state of ethene than with the merely twisted structure previously postulated from theoretical considerations.⁶

¹ R. McDiarmid and E. Charney, J. Chem. Phys. 47, 1517 (1967).

² There are several inconsistent values of frequency differences in Tables I and II of Ref. 1. As the stated average frequencies of that article can be computed only by using these inconsistent values and as they have been deduced to be inconsistent because of the crosscheck in the various columns of the tables, these values are presumed not to represent typographical errors. Apart from five minor errors noted, the serious error in the difference ΔG^1 of the two members 52427 and 53123 of the primary progression of C₂H₄, 796 instead of the correct magnitude 696, means that all later treatment of Ref. 1 is inaccurate quantitatively if not qualitatively. ³ G. Herzberg, Infra-red and Raman Spectra (D. Van Nostrand

Co., Inc., Princeton, N.J., 1960).
⁴ A. D. Walsh, J. Chem. Soc. 1953, 2325.
⁵ F. G. Baglin, S. F. Bush, and J. R. Durig, J. Chem. Phys. 47,

2104 (1967)

⁶ R. S. Mulliken, Phys. Rev. 41, 751 (1932).

Comment on "Electron in Box Theory for Metal-Atom Clusters"

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I have noted certain errors of calculation in Libby's paper on the application of the electron in box model to the metal-atom cluster compounds.¹ The corrected table (agreed to by Professor Libby by correspondence) is given, together with a comparison of Libby's original numbers,¹ in Table I. It is to be noted that the distribution of the numbers of electrons actually found in

TABLE I. Numbers of electrons to fill to successive energy levels.

Flat ($\alpha = 1/2$) This paper Ref. 1		Cube $(\alpha = 1)$ This paper Ref. 1		Square column $(\alpha = 2)$ This paper Ref. 1	
2 6 8 12 16 18 26 28 34 38 46	2 6 8 12 14 22 24 30 34 38 42	2 8 14 20 22 34 40 46	2 8 14 16 28 34 40 46	2 4 6 10 16 20 24 30 36 42 46	2 4 8 14 18 20 26 28 32 36 40
	46				44 48

stable clusters (the italicized numbers 12, 16, 18, 24, 26, and 32) is very different in both cases.

¹ W. F. Libby, J. Chem. Phys. 46, 399 (1967).

Mechanisms of Vibrational Relaxation

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Vibrational relaxation of diatomic molecules has recently been discussed theoretically.¹ We should like to discuss and clarify the mechanisms considered in that work.

The changes in vibrational state of a molecule arise from the interactions of the vibrational coordinate with all other degrees of freedom. The interaction usually considered² is the direct potential energy between the oscillator and the other molecules in the system. For simplicity, this direct potential interaction is usually linearized in the oscillator coordinate, so that the interaction becomes proportional to the force $f_{\rm int}$ exerted on the oscillator by the other molecules. This direct interaction was considered in Sec. II of Ref. 1.

A second force experienced by the oscillator is the centrifugal force due to the rotation of the molecule. When linearized in the vibrational coordinate, this force is

$$f_{\rm cent} = 2E_R/R_0, \tag{1}$$

where R_0 is the equilibrium interatomic distance in the molecule, and E_R is the rotational kinetic energy.³ This contribution has usually been ignored in treating vibrational relaxation. It is just this rotational contribution which was evaluated in Secs. V and VI,¹ and compared in order of magnitude with measurements of vibrational relaxation in Sec. VII.

In general one must include both the intermolecular force f_{int} , and the centrifugal force f_{cent} contributions. Then the total rate of relaxation, calculated as in Ref. 1, becomes

$$W_{n \to n-1} = \frac{nR_0^2}{2I\hbar\omega_0} \int_{-\infty}^{\infty} dt \exp(-i\omega_0 t) \\ \times \langle [f_{\rm int}(0) + f_{\rm cent}(0)] [f_{\rm int}(t) + f_{\rm cent}(t)] \rangle, \quad (2)$$

where I is the moment of inertia and ω_0 is the oscillator frequency. The calculation of the rotational