THEORETICAL VIBRATIONAL SPECTRA AS A TOOL IN THE IDENTIFICATION OF UNUSUAL ORGANIC MOLECULES

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Abstract – Reactive organic systems are often synthesized at low temperature in a frozen matrix and identified by their IR spectra. Typically these are low resolution spectra contaminated by reactants and other products. In such cases theoretical vibrational spectra, computed ab initio, can be of help in the identification and analysis of these spectra. Thus the theoretical IR spectrum of cyclobutadiene is in accord with a rectangular rather than square structure. An experiment that was thought to show the contrary by proving the identity of cyclobutadiene-1,2-d_2 and -1,4-d_2 is reinterpreted as having obtained an equal mixture of these nonequivalent isomers. Similarly revisions are suggested in the interpretation of the observed spectrum of thiirene. In particular, the C–S bond is calculated to be abnormally long and weak, and the corresponding stretching vibration is predicted at unusually low frequency.

INTRODUCTION

As Strausz has pointed out (1), the identification of highly unstable organic molecules usually depends primarily on their IR spectra. Typically, these molecules are formed at low temperature in a frozen matrix. Because of their extreme reactivity, separation and purification are not possible; and the spectra are taken of the frozen reaction mixture. Although Fourier transform techniques have improved the quality of these spectra, the absorptions are broad with unresolved rotational structure; and the spectra are contaminated by other known and unknown reaction products. As a consequence, positive identification of such spectra is difficult. We shall show that theoretically computed vibrational spectra can aid in this problem if the molecule is not too large. At the moment, "too large" would mean more than perhaps 6 or 10 atoms larger than hydrogen.

We were led to the calculation of vibrational spectra by our interest in the theory of aromaticity where cyclobutadiene is a molecule of central importance. Krantz (2) and Chapman (3) had both reported the synthesis of cyclobutadiene by the low temperature photolysis of 2-pyrone. Identification was by the IR spectrum, and the molecule was thought to be square since few bands were observed as would be expected for a structure of such high symmetry. However ab initio calculations of good quality predicted cyclobutadiene should have a rectangular rather than square ground state (4,5). We therefore undertook an ab initio calculation of the vibrational spectrum of cyclobutadiene in hope of finding the calculated spectrum of the rectangular structure to be like the observed spectrum and so resolving the disagreement between theory and experiment.

The variation theorem gives assurance that the error in the wavefunctions used will be such as to give too high an energy, but there is rarely any certain knowledge of how large the error is. Experience suggests that in the cases to be described here the error is probably between 0.1 and 1.0 atomic units (a.u.). An error of even 0.1 a.u. equals 22,000 cm^{-1} which is over 5 times the energy range of the entire IR spectrum. Therefore although we shall obtain computed frequencies accurate to about 100 cm^{-1}, we could not know ahead of time that this would happen. Our approximate potential surfaces will be in error by at least 22,000 cm^{-1}, but it is hoped that they will parallel the true surfaces to a much greater accuracy. Accordingly a preliminary test on a simple molecule of known spectrum seemed prudent. A wavefunction for ethylene was constructed from the relatively primitive STO-4G basis (6) and gave the vibrational frequencies shown in Fig. 1. We had supposed that the experimental
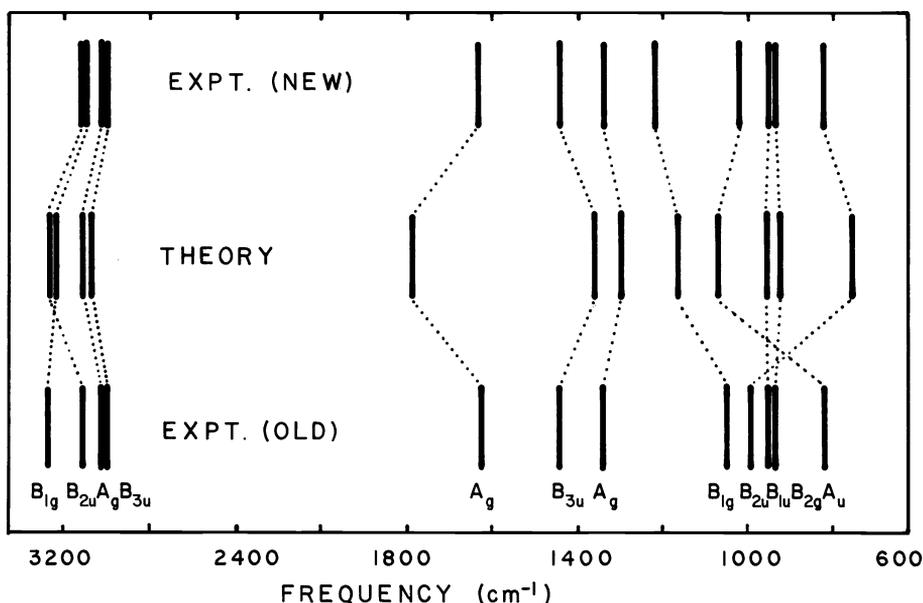
Fig. 1. Comparison of experimental vibrational frequencies of ethylene with those computed using an STO-4G basis. Following Herzberg (Ref. 7), the x axis is that of smallest and the z axis that of largest moment of inertia.

spectrum of a molecule as simple and as common as ethylene must have long been well-known and so compared our ethylene results with those given in Herzberg's book (7). These are labeled "Expt.(old)" in Fig. 1; and, as seen there, do not agree well with our theoretical results. However, there is a more recent experimental study of ethylene (8); and that spectrum, shown as "Expt.(new)" at the top of Fig. 1, does agree exactly in frequency order with our calculated lines. We concluded that had the calculated results been available in 1945 they would have been of help in interpreting the experimental spectrum.

Current IR spectra of the unusual systems to be considered are not more reliable than the 1945 ethylene results. In fact they are worse in one important way. As shown in Fig. 1 symmetry assignments were already made in 1945, though sometimes incorrectly, for all the ethylene fundamentals. Symmetries of calculated lines are given automatically by the calculation, but typically symmetry will not be known for the experimental lines at early stages of a difficult investigation, and this is just where we are hoping calculated spectra will be of use. Without the symmetry labels, the calculated spectrum in Fig. 1 would be of little help in interpreting the experimental results unless the calculated frequencies were much more accurate than they are. Heilbronner (9) has made this same point in regard to photoelectron spectra where he found that randomly generated theoretical spectra fit experiment as well as did typical results from quantum mechanical calculations. The calculated frequencies in Fig. 1 are in error by nearly as much as 200 cm^{-1}. It will be seen that this can be improved but that it will be difficult to decrease the error below about 50 cm^{-1}, still quite large to the experimentalist. With this error and lacking symmetry designations for the experimental lines, calculated vibrational spectra do not appear of much value.

However, in addition to symmetry and frequency, vibrational lines are also characterized by their intensity. For intensity the situation is opposite that for symmetry labels in that it is easy to get at least a rough measure of the experimental intensities in the infrared spectrum, but they do not fall automatically out of the theoretical frequency calculation. Still, they can be calculated without excessive additional work; and Fig. 2 compares calculated and experimental results for the infrared-active vibrations of ethylene. Raman frequencies are not shown since their intensities are somewhat more difficult to calculate, and the corresponding experimental values will not be as readily available for the systems to be considered. Fig. 2 is quite encouraging. The intensity patterns of the calculated and experimental spectra are almost identical, and the experimental lines could be assigned unambiguously using the calculated spectrum. The somewhat better 4-31G basis (10,11) was used in these calculations in place of the STO-4G basis of Fig. 1. With this basis, unlike the STO-4G, all lines are displaced toward higher frequency relative to experiment.

It therefore seems that a theoretical calculation of IR spectra can aid in the interpretation of the experimental spectra of small unusual organic molecules.
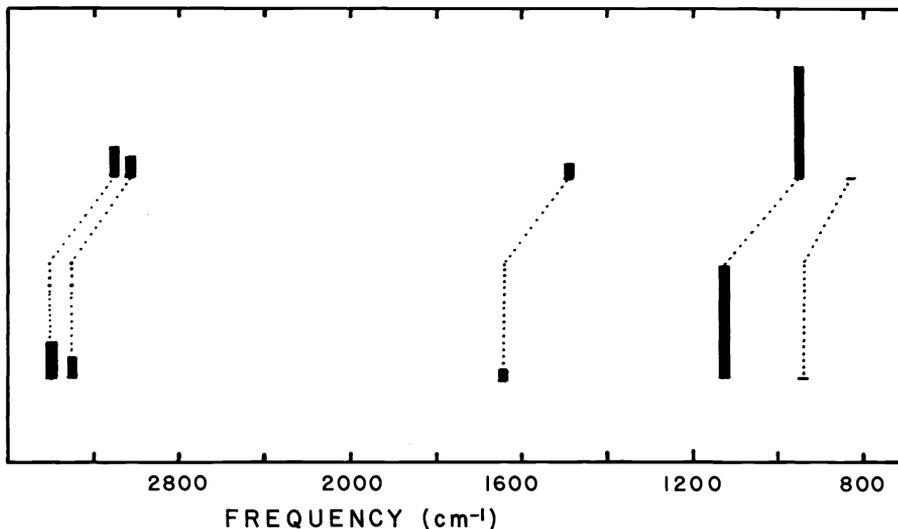
FREQUENCY (cm⁻¹)

Fig. 2. Comparison of experimental (upper) and 4-31G basis theoretical (lower) IR frequencies and relative integrated band intensities of ethylene.

METHOD

Most of our calculations have been done at the LCAO-SCF level with larger or smaller sets of Gaussian basis functions, though in some more recent work electron-electron correlation has been included by the Møller-Plesset perturbation method (12,13). The first step in all cases is to find the molecular geometry corresponding to the minimum energy in the basis set used. The energy of a stationary N-atom molecule depends upon the position of all N atoms. Six (or five for a linear molecule) conditions must be imposed on the 3N Cartesian coordinates of the atoms to ensure that the molecule is neither translating nor rotating in space, leaving 3N-6 coordinates to be varied to give the minimum energy geometry. However such coordinates are strongly coupled, and computationally it is more efficient to describe the molecule in terms of the familiar bond lengths and angles. Some arbitrariness still remains: for example, is it better to describe a 3-membered ring by the lengths of all 3 sides or by 2 sides and an angle? Pulay (14) lists preferred choices for common cases.

Although the internal coordinates (bond lengths and angles) are more practical for actual use, the principles of the vibrational problem are more easily described using the atomic Cartesian coordinates. Let the energy V of the stationary molecule be written as a power series in these Cartesian coordinates x_i expanded about the energy minimum

$$V = V_o + \sum_{i=1}^{3N} \left.\frac{\partial V}{\partial x_i}\right|_o x_i + \frac{1}{2}\sum_{i,j=1}^{3N} \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right|_o x_i x_j + \text{higher order terms} \qquad (1)$$

where the subscript o refers to the minimum-energy configuration. V_o is a constant, and the first derivatives $(\partial V/\partial x_i)|_o$ vanish because of the energy minimization. If higher-order terms are dropped Eq. (1) simplifies to

$$V = V_o + \frac{1}{2}\sum_{i,j} V_{ij} x_i x_j \qquad (2)$$

where V_{ij} is an abbreviation for the second derivative in Eq. (1).

Eq. (2) is the energy of the molecule with all nuclei held at equilibrium. The motion of the nuclei is given by Eq. (3), a Schrödinger equation whose potential is Eq. (2)

$$\left[\sum_{i=1}^{3N}\left(\frac{-\hbar^2}{2m_i}\frac{\partial^2}{\partial x_i^2}\right) + V_o + \frac{1}{2}\sum_{i,j=1}^{3N} V_{ij} x_i x_j\right]\psi = E\psi \qquad (3)$$

Each atom has 3 associated coordinates. Let x_1, x_2 and x_3 be those of the first atom so that $m_1 = m_2 = m_3 =$ the mass of the first atom, and similarly for all atoms. The constant V_o can be taken to the right hand side and combined with the energy E. All variables are separated in the first sum of Eq. (3), but their mixing in pairs in the second sum precludes a simple product solution of Eq. (3). However if a transformation is first made to mass-weighted coordinates $X_i = \sqrt{m_i} x_i$, a further orthogonal transformation from the mass-weighted coordinates X_i to the normal coordinates Q_i can be found such that the potential then contains only diagonal terms

$$\sum_{i,j=1}^{3N} V_{ij} x_i x_j = \sum_{i,j=1}^{3N} \frac{V_{ij}}{\sqrt{m_i m_j}} X_i X_j = \sum_{i=1}^{3N} \lambda_i Q_i^2 \tag{4}$$

With Eq. (4) the Schrödinger equation simplifies to

$$\left[\sum_{i=1}^{3N} \left(\frac{-\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} \right) + \frac{1}{2} \lambda_i Q_i^2 \right] \psi = (E - V_o) \psi \tag{5}$$

The variables in Eq. (5) are entirely separated giving a simple product solution

$$\psi = \psi_1(Q_1) \psi_2(Q_2) \cdots \psi_{3N}(Q_{3N}) \tag{6}$$

where each ψ_i is a solution of

$$\left(\frac{-\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \lambda_i Q_i^2 \right) \psi_i(Q_i) = \varepsilon_i \psi_i(Q_i) \tag{7}$$

Eq. (7) is recognized as the Schrödinger equation for a 1-dimensional harmonic oscillator whose solutions are well known. The vibrational frequency ν (in cycles/sec) is related to the force constant λ by $\nu = \sqrt{\lambda}/2\pi$.

Hence to compute the vibrational frequencies it is first necessary to get the force constants V_{ij} in Eq. (4). The most direct way is to displace the molecule slightly from equilibrium along only one of the coordinates x_i and then to recompute the molecular energy. The increase in V and the known value of x_i give V_{ii}. This is repeated for all coordinates. Then displacements of pairs x_i and x_j give the off-diagonal terms V_{ij}. This straightforward method was used (15-17) in conjunction with the POLYATOM program (18), but in some of the more recent work to be described here we have used the program HONDO (19-22) which computes analytic first derivatives of the energy for use in the optimum geometry search. Force constants were then computed numerically from these analytic first derivatives.

Diagonalization of the force constant matrix $[V_{ij}]$ gives the normal modes Q_i, their eigenvalues λ_i, and the fundamental frequencies ν_i. Using Cartesian x_i, six of these frequencies, corresponding to molecular rotation and translation, should vanish. Small errors due to anharmonicity (i.e. the higher order terms in Eq. (1)) and numerical evaluation of the force constants can make them as large as 80 cm^{-1} instead and suggest at least this large an error in the other computed frequencies.

The intensity of an IR absorption is proportional to the square of the change of the dipole moment $\underline{\mu}$ along the normal mode

$$A_i \propto \left| \frac{\partial \underline{\mu}}{\partial Q_i} \right|^2 = \left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \tag{8}$$

Hence to obtain the intensity the dipole moment is computed at equilibrium and then with the molecule distorted along Q_i.

This description is complicated somewhat on switching from Cartesian to internal coordinates. The main difficulty is that in internal coordinates the first sum in Eq. (1),

which gives the kinetic energy, becomes more elaborate. These difficulties can be treated by the standard Wilson FG matrix method (23) which we are currently using.

RESULTS

The calculated IR spectrum for ethylene discussed above convinced us that a similar calculation for cyclobutadiene could help decide between a square and rectangular structure. As these calculations were being completed, Kollmar and Staemmler (24) published a very similar study. Then at about the same time Masamune's improved spectrum appeared (25). This was interpreted as showing cyclobutadiene not to be square but probably rectangular. Our STO-4G results (15) for rectangular cyclobutadiene agree well with Masamune's data as shown in Fig. 3 together with more recent theoretical spectra from improved wavefunctions.
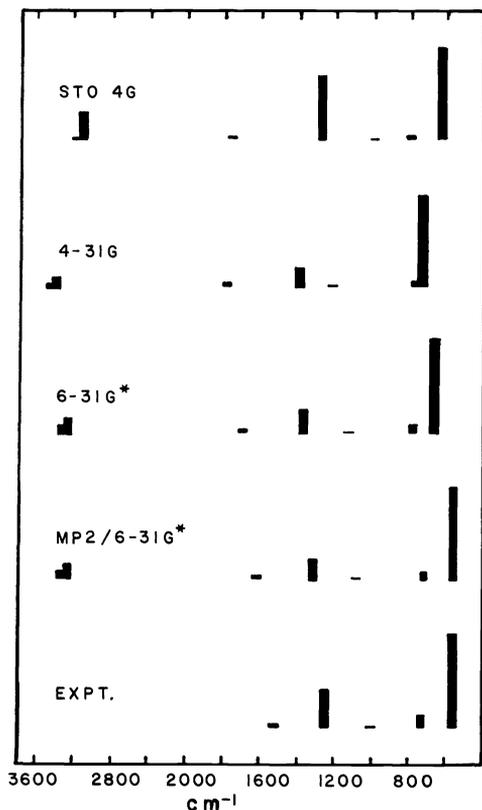

Fig. 3. Calculated and experimental IR spectra of cyclobutadiene. Relative intensities are shown by line heights. The calculations increase in quality from STO-4G to MP2/6-31G*.
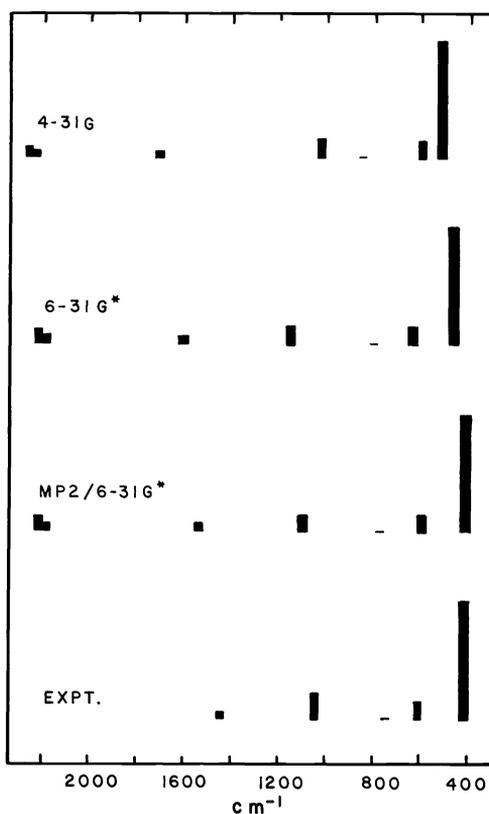
Fig. 4. Calculated and experimental IR spectra of tetradeuteriocyclobutadiene.

The two lines of highest frequency are C-H stretches. These occur in a strongly absorbing region of the experimental spectrum and were not identified by Masamune. Otherwise, even the STO-4G (E = -152.69 a.u.) calculation gives a pattern that agrees well with experiment. Some of the STO-4G frequencies are higher and others lower than experimental. As the wavefunction moves toward the SCF limit with the 4-31G (E = -153.41 a.u.) and 6-31G* (E = -153.64 a.u.) bases all calculated frequencies become higher than experimental. Then when correlation energy is included by the Møller-Plesset method (12) (MP2/6-31G*; E = -154.14 a.u.) all are lowered in frequency toward the experimental values. Fig. 4 compares theoretical and observed IR spectra for rectangular tetradeuteriocyclobutadiene. Again agreement is good and trends are as in Fig. 3.

Thus the experimental spectrum agrees well with that calculated for the rectangular structure. It is natural at this point is to ask whether the theoretical spectrum for a square structure might agree even better. But such a calculation cannot be done in a meaningful way. The square structure is not a theoretical energy minimum, and therefore some of the force constants would be negative and the corresponding frequencies imaginary.

This agreement between theory and experiment on the rectangular structure of cyclobutadiene leaves one earlier experiment unexplained. In 1973 Chapman, De La Cruz, Roth and Pacansky (26) synthesized dideuteriocyclobutadiene from 2-pyrone-5,6-d_2
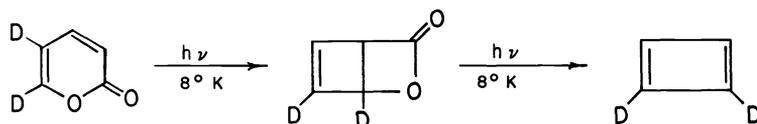
and from 2-pyrone-3,6-d_2
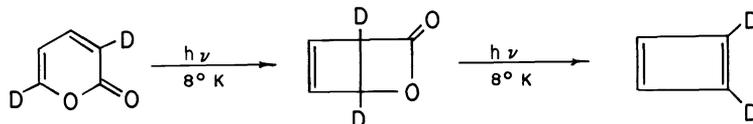
If cyclobutadiene is rectangular the two d_2 isomers should be distinct and give different IR spectra. Chapman found the same spectrum in both cases. This is consistent with a square structure for cyclobutadiene, but apparently not with a rectangular structure.

Spectral intensities were not given in Chapman's short paper, but they are available in De La Cruz' thesis (27) together with an improved spectrum. Frequencies and intensities taken from this are shown at the bottom of Fig. 5. Clearly, the calculated spectrum for neither
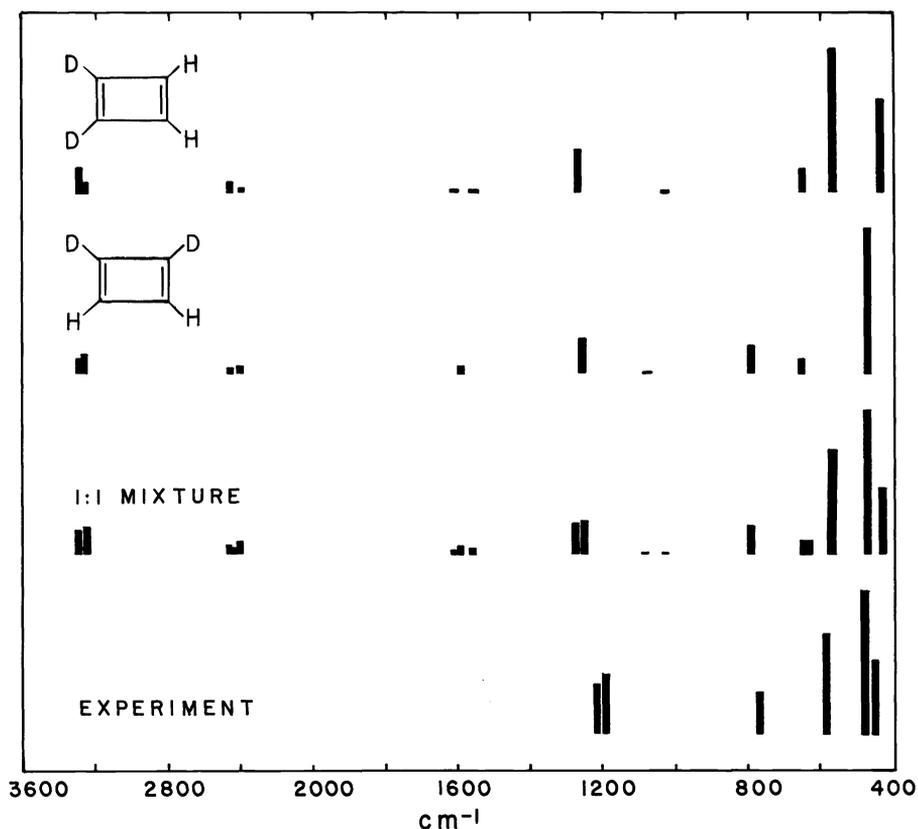

Fig. 5. Experimental IR spectrum observed by Chapman and coworkers (Refs. 26 and 27) and computed MP2/6-31G* spectra for cyclobutadiene-1,2-d_2, cyclobutadiene-1,4-d_2 and a 1:1 mixture.

cyclobutadiene-1,2-d_2 (with D atoms adjacent across the double bond) nor cyclobutadiene-1,4-d_2 (D atoms across the single bond) looks like the experimental result. As seen in Fig. 5 there are more strong absorptions below 1500 cm^{-1} than predicted for either isomer. However the theoretical spectrum for a 1:1 mixture of the two isomers agrees quite well with experiment. This suggests strongly that Chapman observed a mixture of the two distinct

isomers in both experiments and provides further support for the rectangular structure of cyclobutadiene.

The thiirene molecule (1) is another small highly reactive molecule synthesized in a frozen

$$
\underset{\textbf{1}}{
HC \overset{\displaystyle \overset{\textstyle S}{\diagup \ \diagdown}}{=\!=\!=} CH
}
$$
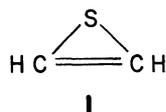
matrix and identified by its IR spectrum (28,29). Although it has only been known a short time, there have already been several changes in its assigned experimental spectrum. It is instructive to follow these changes in comparison with our calculated spectrum (16). Figure 6 shows the four steps in this evolution, with experimental spectra above and the same 4-31G
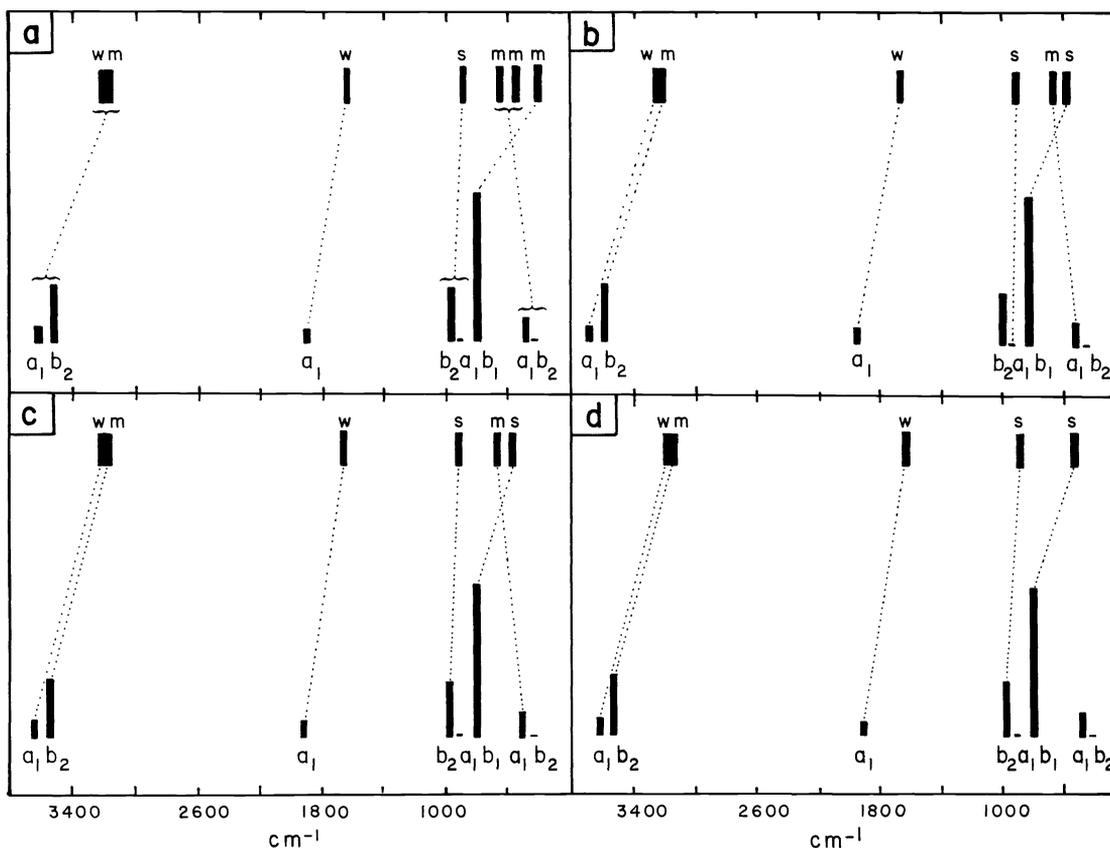

Fig. 6. The theoretical 4-31G IR spectrum (below in each section) of thiirene compared with the evolving experimental results (above in each section).

theoretical spectrum below in each of the sections. Figure 6a is from the original spectrum published by Strausz and coworkers (29). Intensities are given only as strong, medium or weak, and only the coarsest details of the observed spectrum have been assigned. The two C-H stretches, the C=C stretch and one C-H in-plane bend do correspond to our calculations; but at longer wavelengths there is not agreement between observed and calculated lines.

More recently this group has published a revised spectrum (30) as in Fig. 6b. The two C-H stretches have been assigned individually and agree with ours, both in relative intensity and position; but the strong band near 1000 cm^{-1} has been assigned to the a_1 C-H bend which we calculate to be much weaker than the b_2 band. Disagreement remains at longer wavelengths, although one of the earlier experimental bands here has now been dropped.

Still more recently Strausz (1) has revised the assignment of the C-H in-plane bend to b_2 rather than a_1, giving the correspondence in Fig. 6c. Finally, Krantz and Laureni (28,31) question the origin of the observed 657 cm^{-1} band. This band exists in the experimental spectrum; but its rate of appearance, and hence whether or not it is due to thiirene, are

difficult to determine. Strausz assigns this band to a symmetric ring deformation which must be due largely to a stretching of the C-S bonds. We compute this C-S stretch should lie much lower at 478 cm^{-1}. The Strausz assignment is in analogy with the C-S stretch in thiirane (32) which appears at 627 cm^{-1}. However, as seen, the tendency is for the theoretical predictions to be too high in frequency. Further the C-S bond in thiirene is calculated to be long and weak so that thiirene might be thought of as a sulfur atom in loose association with an acetylene molecule (33). We might therefore expect the C-S stretch in thiirene to lie below, not above, that in thiirane. If then the 657 cm^{-1} band is dropped, experimental and calculated spectra correspond fairly well as shown in Fig. 6d. The three highest frequency bands are in agreement. Of the five low-frequency bands, the two calculated to be most intense have been observed. Of the three remaining, that of predicted highest intensity is the a_1 C-S stretch which should lie lower in frequency than the observed bands. The a_1 in-plane C-H bend and the b_2 ring deformation are of low computed intensity and should be difficult to observe.

Theoretical spectra of several D and ^{13}C isotopically substituted thiirenes have also been obtained as have those for the as yet unknown oxirene and azirene (33).

From the examples given it is seen that while finer details of the theoretical vibrational spectrum are not to be trusted, the overall pattern is remarkably accurate and can aid, not just in the identification of new species, but also in the interpretation of their experimental spectra.

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