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Absolute Infrared Intensities of Hydrocarbons

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Dipole-moment derivatives, calculated by both the CNDO/2 method with different parameterizations and the INDO method, are compared to the experimental values determined from absolute infrared intensity measurements for the IR active modes of methane, ethane, ethylene and acetylene. A parameter refinement procedure is introduced in which the CNDO/2 molecular orbital parameters are adjusted through a damped least-squares treatment to give best agreement with the observed dipole-moment derivatives. It is found that the refinement does not substantially improve the agreement obtained with the original CNDO/2 parameterization. The INDO method gives somewhat poorer agreement than the CNDO/2 calculations. As an example of the applicability of the molecular orbital methods toward reproducing relative infrared intensities, the spectrum of cyclopropane in the gas-phase is examined.

Die Ableitungen des Dipol-Moments, die nach der CNDO/2-Methode mit verschiedenen Parametrisierungen sowie der INDO-Methode berechnet wurden, werden mit den experimentellen Ergebnissen aus Messungen der absoluten Infrarot-Intensitäten für die IR-aktiven Schwingungen von Methan, Äthan, Äthylen und Azetylen verglichen. Die CNDO/2-Parameter werden mit einer Methode der kleinsten Quadrate den beobachteten Dipol-Moment-Ableitungen angepaßt. Die Ergebnisse sind jedoch nicht wesentlich von denen der ursprünglichen CNDO/2-Methode verschieden. Die INDO-Ergebnisse sind nicht so gut wie die CNDO/2-Ergebnisse. Als Beispiel der Anwendbarkeit der MO-Methoden zur Berechnung von relativen IR-Intensitäten wird das Spektrum des Cyclopropans in der Gasphase untersucht.

Les dérivées du moment dipolaire, calculées par la méthode CNDO/2 avec différentes paramétrisations et par la méthode INDO, sont comparées aux valeurs expérimentales déterminées à partir de mesures d'intensité absolue pour les modes actifs dans l'infra-rouge dans le méthane, l'éthane, l'éthylène et l'acétylène. Les paramètres sont ajustés de manière à donner le meilleur accord avec les dérivées du moment dipolaire. Cet ajustement n'améliore pas sensiblement l'accord obtenu avec la paramétrisation CNDO/2 originale. La méthode INDO donne des résultats moins bons que les calculs CNDO/2. Le spectre du cyclopropane en phase gazeuse est étudié comme exemple de l'applicabilité de la méthode des orbitales moléculaires au calcul des intensités relatives infra-rouge.

Introduction

Applications of the empirical relations between molecular structure and the properties derived from vibrational spectroscopy appear widely in diverse areas of organic chemistry. In particular, the concept of characteristic group vibrations has led to extensive correlations between vibrational frequencies and intramolecular motions for innumerable classes of compounds [1–3]. More recently, both an understanding of the origins of these group frequencies and an insight into the electronic structure of organic systems have been achieved through the development of force field computations for moderately large molecules [4, 5]. The use of these intramolecular potential functions to provide a means of successfully predicting the conformational minima for molecular systems reflects an example of a significant area in which vibrational frequency information has been utilized [6].

The absolute infrared band intensity, which arises from the dipole-moment derivatives generated in a vibrating system, represents a second important type of vibrational data derived from infrared spectra. The applications of intensity measurements closely parallel those for frequency data. For example, empirical tabulations of absolute band intensities are useful in structural determinations for a variety of functional groups [7]. The second step, however, of relating the experimental intensity measurements to bond properties has received generally less attention and has been largely ignored by the organic chemist [8, 9]. Thus, in order to derive the maximum information from an infrared spectrum, it is necessary to understand the relation of infrared intensities to the charge redistributions in vibrating systems. This spectroscopic area, which is the subject of the present study, appears promising in that an understanding of the charge redistributions associated with various molecular motions is of fundamental importance in elucidating chemical behaviour and reaction mechanisms.

In relating absolute infrared intensity data to meaningful molecular parameters, recent calculative approaches consider two distinct methods: the group moment model [10] and the application of molecular orbital procedures [11–15]. In the group moment interpretation, Snyder [10] has assumed the transferability of a set of dipole-moment derivatives $\boldsymbol{p}_j$ ($\boldsymbol{p}_j \equiv \partial \boldsymbol{P}/\partial S_j$, where $\boldsymbol{P}$ and S_j represent a group dipole moment and a group symmetry coordinate, respectively) for a series of *n*-alkanes. Using a least squares technique, he refines a set of $\boldsymbol{p}_j$ about a large number of integrated intensity values and finds that he can account quite well for the observed data. In the second approach [11–15], the semi-empirical CNDO/2 molecular orbital method has been applied toward calculating directly the change in dipole moment as a function of the displacement coordinates. In the present study we investigate the INDO method [16] as well as the CNDO/2 method with a modified parameterization in attempts to achieve the best agreement between experimental and calculated infrared intensities for a series of hydrocarbons. In addition, we examine the applicability of molecular orbital procedures toward reproducing relative infrared intensities for organic species. The latter aspect is illustrated by a calculation of the infrared spectrum of cyclopropane.

Infrared Intensities

The absolute intensity Γ_i of an infrared band i is experimentally derived from the integrated absorption coefficent α_ν [8]:

$$\Gamma_i = \int_{\text{band}_i} \alpha_\nu \, \mathrm{d}ln\nu = \frac{1}{nl} \int_{\text{band}_i} ln(I_0/I) \, \mathrm{d}ln\nu , \qquad (1)$$

where I_0 and I are the incident and transmitted intensities at a frequency ν, n represents the sample concentration, and l is the cell path length. The experimental intensity is related to molecular parameters through Eq. (2) [17],

$$\Gamma_i = \frac{N\pi d_i}{3c^2\omega_i}\left(\frac{\partial \boldsymbol{P}}{\partial Q_i}\right)^2, \tag{2}$$

where $\partial \boldsymbol{P}/\partial Q_i$ represents the dipole-moment derivative with respect to the excited normal coordinate Q_i; d_i is the degeneracy of band i with harmonic frequency ω_i; N is Avogadro's number. Since the Q_i represent unspecified normal coordinates, a transformation is desired to express the dipole-moment derivatives in terms of specified symmetry coordinates. One writes the symmetry coordinates S_j as symmetry determined combinations of internal coordinates r_i and α_i, bond stretching and bond bending displacements, respectively. The desired dipole-moment gradients with respect to symmetry coordinates $\partial \boldsymbol{P}/\partial S_j$ are then determined as follows [18]:

$$\frac{\partial \boldsymbol{P}}{\partial S_j} = \sum_i (L^{-1})_{ij}(\partial \boldsymbol{P}/\partial Q_i). \tag{3}$$

The transformation coefficients L_{ji} represent the normal coordinate vectors that are obtained from a complete molecular vibrational analysis.

Semiempirical all-valence electron molecular orbital calculations allow a determination of the dipole-moment derivatives for molecules of reasonable size. The molecule is distorted along a symmetry coordinate S_j and the dipole-moment derivative $\boldsymbol{p}_j$ is calculated as the slope of the change in dipole moment with respect to the symmetry distortion about the equilibrium conformation. The calculated $\boldsymbol{p}_j$ values are compared with the experimental values derived through Eq. (3). Alternatively, they may be utilized for direct comparison with the infrared band intensities Γ_i through use of Eqs. (4) and (2):

$$\frac{\partial \boldsymbol{P}}{\partial Q_i} = \sum_j L_{ji}\frac{\partial \boldsymbol{P}}{\partial S_j}. \tag{4}$$

The $\partial \boldsymbol{P}/\partial Q_i$ obtained from experimental Γ_i by Eq. (2) contain an ambiguity in the absolute sign. Therefore, 2^{n-1} different absolute values arise for the $\boldsymbol{p}_j$ derived from Eq. (3), where n is the number of vibrations for a particular symmetry species. In an *a priori* calculation of $\boldsymbol{p}_j$, the absolute signs of the dipole moment derivatives are computed directly. The calculation may then be used to select the correct set of $\boldsymbol{p}_j$ from the several possible experimental sets for each symmetry species. Therefore, one depends on calculations to yield both the correct magnitudes and signs for the dipole-moment derivatives.

Calculations

The CNDO/2 [19] and INDO [16] molecular orbital methods have been described in detail in the literature. The molecular dipole moment is calculated as the sum of an atomic charge densities term and an atomic *sp* polarization term. For our calculations, we have used modified versions of programs written by Segal and Dobosh and made available through the Quantum Chemistry Program Exchange, University of Indiana. Dipole-moment derivatives were calculated by deforming molecules from their equilibrium geometries and computing the dipole-moment gradients for the particular symmetry distortions[1]. Calculations were made for increments of ± 0.01 or ± 0.02 Å for the stretching coordinates and for increments of ± 1° or ± 2° for the bending coordinates. This procedure is the same as that described by Segal and Klein [11].

All experimental dipole-moment derivatives, obtained from the literature and listed in Table 1, were determined from gas-phase infrared measurements using high broadening pressures of an infrared inert gas. Consequently, these dipole gradients reflect experimental errors of no more than 10–15%. Since data were available for a number of simple hydrocarbons, we felt that absolute infrared intensities were ideal for refinement of the molecular orbital parameterization for carbon and hydrogen. Since infrared intensities are sensitive functions of electronic distributions, any calculation which produces good agreement with experimental intensities should accurately reflect molecular electronic structures.

For the refinement of the CNDO/2 parameterization for the optimum calculation of infrared intensities, we adapted a least-squares model fitting program made available by the Division of Computer Research and Technology of the National Institutes of Health. This program, combined with the CNDO/2 program, systematically adjusted the CNDO/2 parameters for best agreement with the experimental intensities. Dipole-moment changes were calculated at only one distorted geometry (+ 0.02 Å for stretches and + 2° for bends, except for the ethane bending modes, where + 1° increments were taken). S_{12} of ethylene was not included in the parameter refinement because of our uncertainty regarding the relative sign for the dipole-moment derivative (vide infra). The other thirteen symmetry modes listed in Table 1 were used in the refinement. The adjusted molecular orbital parameters are indicated in Table 2. The least-squares refinement proceeded initially from the Pople-Segal parameterization [19].

Several molecular orbital adjustment procedures have previously been discussed in the literature in connection with infrared intensities. For example, King [20] and Coulson and coworkers [21–22] determined p_j for particular systems from empirically chosen wave functions containing adjustable parameters characteristic of the individual molecule and vibrational mode. Although unconcerned with infrared intensity calculations, Wiberg [23] recently considered the specific variation of the CNDO/2 parameters; namely, he applied a random number generator in adjusting the parameters to minimize the deviations between calculated and experimental hydrocarbon energies and equilibrium geometries. Brown and Burden [24] have optimized core hamiltonian matrix elements for the CNDO method by the method of least-squares to obtain best agreement with experimental dipole-moments for a large number of molecules. The rationale for any of these treatments, of course, is that when atomic and molecular integrals are evaluated empirically, it is not clear whether one has selected the best empirical values. This question may be examined by variation of the molecular orbital

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[1] Experimental geometries were obtained from the literature as follows: methane and acetylene, Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London (1965); ethane, Allen, Jr., H. C., Plyler, E. K.: J. chem. Physics **31**, 1062 (1959); ethylene, Bartell, L. S., Bonham, R. S.: J. chem. Physics **31**, 400 (1959); cyclopropane, Jones, W. H., Stoicheff, B. P.: Canad. J. Physics **42**, 2259 (1964). The symmetry distortions used were those defined in connection with the force field computations performed on these systems. Table 1 contains these references.

Table 1. *Comparison between calculated and observed dipole-moment derivatives p_j. The units of p_j are debyes per angstrom*

Species		Vibration		CNDO/2	INDO	Wiberg CNDO/2	Refined CNDO/2	Observed p_j[a]
CH_4	F_2	S_3	Stretch	−0.626	−0.791	−0.388	−0.547	±0.704
		S_4	Bend	0.241	0.023	0.597	0.254	∓0.387
C_2H_6	A_{2u}	S_5	Stretch	0.828	0.956	0.632	0.614	±1.013
		S_6	Bend	0.118	−0.089	0.441	0.143	±0.374
	E_u	S_7	Stretch	1.867	2.221	1.283	1.473	±1.221
		S_8	Bend	−0.198	−0.384	+0.165	−0.103	∓0.295
		S_9	Bend	0.645	0.564	0.746	0.482	±0.418
C_2H_4	B_{1u}	S_7	Bend	2.368	1.759	2.112	2.719	1.805
	B_{2u}	S_9	Stretch	−1.232	−1.480	−0.866	−0.845	±0.725
		S_{10}	Bend	−0.392	−0.255	−0.723	−0.236	±0.350
	B_{3u}	S_{11}	Stretch	0.859	1.026	0.777	0.505	±0.605 (±0.580)[b]
		S_{12}	Bend	0.043	−0.137	0.296	0.145	∓0.269 (±0.365)
C_2H_2	Σ_u^+	S_3	Stretch	0.340	0.082	0.115	1.156	1.228
	π_u	S_5	Bend	−0.801	−0.691	−0.586	−0.935	1.482
Root-mean-square percent deviation				46.8	68.8	69.7	36.7	

[a] Observed values were obtained from the following references. CH_4: Heicklen, J.: Spectrochimica Acta **17**, 201 (1961); C_2H_6: Nyquist, I. M., Mills, I. M., Person, W. B., Crawford, B., Jr.: J. chem. Physics **26**, 552 (1957); C_2H_4: Ref. [28]; C_2H_2: Eggers, D. F., Hisatsune, I. C., Van Alten, J.: J. physic. Chem. **59**, 1124 (1955).

[b] Alternative sign combination of the B_{3u} species. Ref. [28].

Table 2. CNDO/2 *parameters determined from dipole-moment derivative refinement*[a]. *Pople-Segal parameters appear in parentheses*[b]

Orbital	1/2 $(I + A)$	Slater exponent	β Proportionality constant
H, 1*S*	6.1430 (7.1761)	1.3019 (1.2)	6.5280 (9.0)
C, 2*S*	12.410 (14.051)	1.7846 (1.625)	18.664 (21.0)
C, 2*P*	5.5488 (5.572)	1.7846 (1.625)	18.664 (21.0)

[a] The observed dipole-moment derivatives for the following vibrational modes were used in the refinement: CH_4 (S_3, S_4), C_2H_6 (S_5, S_6, S_7, S_8, S_9), C_2H_4 (S_7, S_9, S_{10}, S_{11}), C_2H_2 (S_3, S_5).

[b] Ref. [19].

parameterization to achieve best agreement with a desired experimental property. Therefore, we utilize a fitting procedure in which the CNDO/2 parameters are systematically varied by the method of damped least squares, an iterative technique in which the squares of the residuals between the calculated and observed intensities and the squares of the parameter corrections are simultaneously minimized in each cycle [25]. This method is analogous to the familiar force field adjustment algorithm with the addition of a variable damping factor for avoiding the relatively common occurrence of ill-conditioning of the normal equations [26].

In matrix notation, the least-squares procedure involves the determination of a correction vector $\boldsymbol{\delta}$ to the CNDO/2 parameters. This vector $\boldsymbol{\delta}$ is defined by Eq. (5) [27]:

$$\boldsymbol{\delta} = (J'WJ - \varepsilon)^{-1} J'W\Delta(\partial \boldsymbol{P}) \tag{5}$$

where J represents the Jacobian matrix of the calculated dipole-moment changes with respect to the CNDO/2 parameters; $\Delta(\partial \boldsymbol{P})$ is the vector of differences between the observed and calculated dipole-moment changes; W is a weight matrix which has been arbitrarily taken as a unit matrix. The damping factor ε is chosen by the program, following Levenberg's procedure [25], and aids in achieving rapid convergence. The correction vector is added to the parameter vector in each cycle with the procedure repeated until convergence. Dispersions for the best parameter estimates are given by the moment matrix $\boldsymbol{\sigma}$ [27]:

$$\boldsymbol{\sigma} = ((J'WJ)_{jj}^{-1})^{\frac{1}{2}} \left(\frac{\Delta(\partial \boldsymbol{P})}{n} \right)^{\frac{1}{2}}, \tag{6}$$

where n is the number of observables.

Results and Discussion

Table 1 lists the calculated and experimental dipole-moment derivatives for the infrared active symmetry modes of methane, ethane, ethylene, and acetylene. The calculated values have been obtained using the CNDO/2 method with three different parameterizations and the INDO method. Agreement between the calculated and experimental dipole-moment derivatives may be evaluated by referring to the root-mean-square percent errors given in Table 1 for the various calculative methods. These percent errors have been computed without including the S_{12} bending deformation of ethylene. Agreement between calculation and experiment is very poor for this motion, and it leads to three out of the five incorrect relative sign predictions for the dipole-moment derivatives in Table 1. This poor agreement has led us to speculate on the validity of the sign combination chosen by Golike *et al.* [28] for the B_{3u} species of ethylene. This combination was chosen to give the best agreement with the intensity data for the isotopic derivatives, although it leads to contradictions for the interpretation of the ethylene intensities using a bond moment model [28]. The alternative choice for the B_{3u} combinations of dipole-moment derivatives is indicated in parentheses in Table 1. This combination avoids the sign ambiguity that arises in the bond moment interpretation and clearly seems to be favoured by molecular orbital calculations.

The only other incorrect predictions of relative sign combinations occur with the INDO method for the A_{2u} species of ethane and with the Wiberg parameterization for the E_u species of ethane where the signs for the S_6 and S_8 dipole-moment derivatives are apparently calculated incorrectly. These three modes, S_{12} of ethylene and S_6 and S_8 of ethane, where several discrepancies are encountered, all involve cases where the experimental dipole-moment derivative is relatively small. They involve similar motions, since each corresponds to a bending symmetry mode in which bond angles around one carbon expand and those around the other contract. The calculated dipole moment derivatives for each of these motions arise from approximately equal contributions of opposite sign from the charge densities and atomic polarization terms. Segal and Klein have noted that such a cancellation of contributions may lead to incorrect sign predictions [11].

It is clear from Table 1 that in the overwhelming majority of cases the calculations have reproduced quite well the relative signs and magnitudes of the dipole moment derivatives. With the root-mean-square percent deviations as a means of comparison, agreement between calculation and experiment is best for the CNDO/2 method with the refined parameterization, although the improvement over the Pople-Segal parameterization is certainly not large. Although the number of dipole-moment derivatives used in the refinement is too small for a strict statistical analysis, the standard errors obtained from the least-squares moment matrices (Eq. (6)) indicate a general idea of the sensitivity of the dipole-moment derivative fit to the refined CNDO/2 parameters. The fit appears to be most sensitive to the β proportionality constant for carbon, the average ionization potential for the carbon 2*s* orbital and the Slater exponent for carbon. The least sensitive parameters to the refinement are the β proportionality constant for hydrogen, the average ionization potential for hydrogen and the average ionization potential for the carbon 2*p* orbital. Analysis of the correlation matrix, however, indicates that β for H 1*s* and the average I.P. for C 2*p* and the average I.P.'s for H 1*s* and C 2*p* are strongly correlated, which probably accounts for their larger dispersions.

In a comparison between the four parameterizations for obtaining dipole-moment derivatives, Table 1 indicates that the INDO and Wiberg methods are somewhat worse than the Pople-Segal and the refined treatments. The small overall improvement obtained with the refined parameterization is certainly not substantial enough to warrant wider use. Since an examination of parameter values in Table 2 indicates relatively small changes from the Pople-Segal values, the results may be interpreted as further evidence of the accuracy with which the original CNDO/2 method reproduces both charge distributions and redistributions. The refinement procedure represents a systematic test of this capability and, perhaps, would have been more successful in improving the agreement between theory and experiment with another property or molecular orbital method.

Several generalizations may be made regarding the charge reorganizations accompanying various molecular motions. As noted by Segal and Klein [11], the electronic redistributions arise from changes in atomic hybridizations; and in this respect, the trends indicated by the calculations are in accord with chemical intuition. On stretching carbon-hydrogen bonds, there is a shift of the charge density toward hydrogen, and on contraction, the charge goes to the carbon atom. This is what one expects from decreased *s* character in the carbon hybrid-orbital on lengthening the bond and increased *s* character on contraction. The calculations confirm that this is occurring and 1*s*–2*s* carbon-hydrogen bond indices[2]

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[2] The bond index between two atomic orbitals *a* and *b* is defined by Wiberg (Wiberg, K. B.: Tetrahedron **24**, 1083 (1968)) as the square of the bond order p_{ab}^2. This quantity measures the amount of charge in atomic orbital *a* involved in bonding to orbital *b*. It has been used to estimate hybridization in CH bonds and has been correlated with $J(^{13}\mathrm{CH})$ coupling constants. The relation of bond indices to hybridization has been discussed by Trindle and Sinanoğlu (Trindle, C., Sinanoğlu, O.: J. Amer. chem. Soc. **91**, 853 (1969)).

may be utilized to examine hybridization effects. For example, the S_3 methane stretching mode involves an expansion of two of the carbon-hydrogen bonds and a contraction of the other two. For 0.02 Å deformations, using the CNDO/2 method with the $P-S$ parameterization, the charge density on the expanded hydrogens is 0.9891 and on the contracted hydrogens 0.9857; the charge on hydrogen in the equilibrium conformation is 0.9874. The 1*s*–2*s* carbon hydrogen bond index for the equilibrium conformation is 0.249 corresponding to 24.9% *s* character in the carbon hybrid orbital. For the S_3 motion this 1*s*–2*s* bond index becomes 0.244 for the expanded hydrogens and 0.254 for the contracted hydrogens which corresponds to a decreased *s* character and an increased *s* character, respectively. This rehybridization effect is observed for all the carbon hydrogen bond stretching deformations that we calculated, but the magnitude of the effect decreases with increasing *s* character in the original carbon hybrid orbitals. Thus, for the S_3 mode of acetylene, in which one C–H bond is expanded and the other contracted, the C–H 1*s*–2*s* bond indices are 0.434 for the expanded and 0.440 for the contracted hydrogens. This is compared to 0.437 in the equilibrium conformation. The charge redistributions are correspondingly smaller.

Rehybridization effects also accompany bending distortions. As the bond angle around carbon is expanded, more *s* character enters the hybrid orbitals. The S_4 bending distortion of methane involves expansion of one HCH angle for one pair of hydrogens and contraction of the HCH angle for the other pair. The hydrogen charge for a 2° angle deformation goes from the equlibrium value of 0.9874 to 0.9863 for hydrogens around the expanded angle and to 0.9886 for hydrogens around the contracted angle. The equilibrium value of 0.249 for the C–H 1*s*–2*s* bond index becomes 0.254 for the hydrogen around the expanded angle and 0.244 for the hydrogens around the contracted angle. Again, the rehybridization becomes smaller, as the *s* character increases in the original carbon hybrid orbital.

Application to Cyclopropane

In this section, we apply molecular orbital methods toward computing the *relative* infrared intensity features of a molecule in the gas phase. For several reasons, we chose the cyclopropane molecule as the example for this application. First, the absorption bands for cyclopropane are not seriously overlapped and thus a comparison between calculated and observed spectra is facilitated. Also, reliable frequency and Coriolis data were available for cyclopropane and several deuterated derivatives such that a complete force field analysis could be determined [29, 30]. Moreover, cyclopropane represents a highly strained system and serves as a further test of the general applicability of molecular orbital methods for the calculation of infrared intensities of hydrocarbons.

Cyclopropane exhibits six infrared active bands, ν_6 and ν_7 of the A_2'' symmetry species and ν_8, ν_9, ν_{10} and ν_{11} of the E' symmetry species. The top portion of Fig. 1 displays the spectrum of C_3H_6 obtained in a 10-cm gas cell. The relative intensities of the fundamental modes are represented by a bar graph with the length of the lines proportional to the areas under the absorption bands. The relative areas were obtained from expanded infrared traces with a planimeter and are

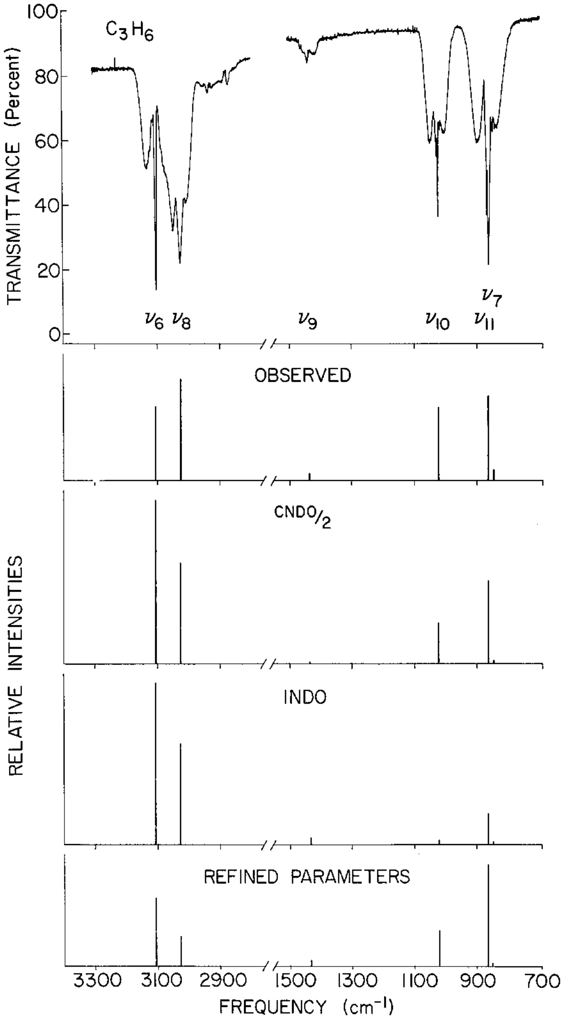

Fig. 1. Observed and calculated relative infrared intensities for gaseous cyclopropane

given in Fig. 1 for the bar graph labeled "observed." In order to obtain band areas for the overlapping bands corresponding to ν_6 and ν_8 and ν_7 and ν_{11}, graphical separations were made. The procedure was subject to only a small error for the separation of ν_6 and ν_8, but is more arbitrary for the ν_7 separation.

The dipole-moment derivatives for symmetry distortions, defined by Duncan and Burns [30], were calculated by the CNDO/2 method with both the Pople-Segal and the refined parameterizations and by the INDO method. The band intensity is obtained from Eqs. (4) and (2). Since Eq. (4) requires the normal coordinate vectors obtained from a complete force field analysis, we used the *L* matrices of Duncan and Burns [30]. The *L* matrix for the *E′* species is highly reliable as both normal and deuterium frequencies and Coriolis ζ-constants were used in the statistical refinement of the force field. Since a sensitive force field constraint is not available for the A_2'' species, the L matrix for this species is not as well defined. Moreover, in the force field refinement for the A_2'' species, the off diagonal F matrix elements were constrained to zero, which, therefore, limits the validity of the derived normal coordinates.

Intensities shown in Fig. 1 for the CNDO/2 and INDO schemes were normalized to ν_8 and those shown for the CNDO/2 method with the refined parameterization were normalized to ν_{11}. The agreement between the observed and calculated relative intensities in Fig. 1 is quite good. The ν_9 and ν_7 modes are correctly predicted to be of low intensity and the relative intensities for other bands are qualitatively correct. The most satisfactory agreement with the observed values seems to be for the intensities calculated by the CNDO/2 method with the Pople-Segal parameterization. In all methods, however, the ν_6 mode is calculated to be more intense than the ν_8 mode. Since the band assigments are beyond question, this result may reflect the approximation used to derive the L matrix for the A_2'' species, which would propagate an error to the calculated value for the ν_6 intensity.

It should be emphasized that our comparison has been with observed relative infrared intensities with no band broadening by an infrared inert gas. It is likely, therefore, that intensity is lost in the sharp Q branches for some of the bands because of limited spectral resolution. (Spectra were run on a Perkin-Elmer Model 521 spectrophotometer at spectral slitwidths varying from 0.7 to 1.0 cm^{-1}.) We intend to examine the *absolute* infrared band intensities for cyclopropane both for a more detailed comparison with molecular orbital calculations and for examination of absolute intensities as a constraint on the force field, particularly with regard to the A_2'' species.

References

1. Bellamy, L. J.: The infrared spectra of complex molecules. London: Methuen and Co., Ltd. 1954.
2. — Advances in infrared group frequencies. London: Methuen and Co., Ltd. 1968.
3. Colthup, N. B., Daly, L. H., Wiberly, S. E.: Introduction to infrared and raman spectroscopy. New York: Academic Press 1964.
4. Snyder, R. G., Schachtschneider, J. H.: Spectrochimica Acta **19**, 85 (1963).
5. Califano, S.: Pure appl. Chem. **18**, 353 (1969).
6. Williams, J. E., Strong, P. J., von R. Schleyer, P.: Annu. Rev. physic. Chem. **19**, 531 (1968).
7. Wexler, A. S.: Appl. Spectroscopy Rev. **1**, 30 (1967).
8. Overend, J.: Infrared spectroscopy and molecular structure, ed. by M. Davies, p. 345. Amsterdam: Elsevier 1963.
9. Steele, D.: Quart. Rev. **18**, 21 (1964).
10. Snyder, R. G.: J. chem. Physics **42**, 1744 (1965).
11. Segal, G. A., Klein, M. L.: J. chem. Physics **47**, 4236 (1967).
12. Bruns, R. E., Person, W. B.: 24th Symposium on molecular structure and spectroscopy. Paper M 5. The Ohio State University, Columbus, Ohio, September 1969.
13. Segal, G. A., Bruns, R. E., Person, W. B.: J. chem. Physics **50**, 3811 (1969).
14. Brownlee, R. T. C., Katritzky, A. R., Sinnot, M. V., Szafran, M., Yakhontov, L., Topsom, R. D.: Tetrahedron Letters 5773 (1968).
15. Levin, I. W., Lewis, T. P.: J. chem. Physics. **52**, 1608 (1970).
16. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. chem. Physics **47**, 2026 (1967).
17. Crawford, B. L., Jr.: J. chem. Physics **29**, 1042 (1958).
18. Wilson, E. B., Jr., Decius, J. C., Cross, P. G.: Molecular vibrations. New York: McGraw-Hill Book Co., Inc. 1955.

19. Pople, J. A., Segal, G. A.: J. chem. Physics **44**, 3289 (1966).
20. King, W. T.: J. chem. Physics **39**, 2141 (1963).
21. Coulson, C. A., Stephen, M. J.: Trans. Faraday Soc. **53**, 272 (1957).
22. Cohen, N. V., Coulson, C. A.: Trans. Faraday Soc. **52**, 1163 (1956).
23. Wiberg, K. B.: J. Amer. chem. Soc. **90**, 59 (1968).
24. Brown, R. D., Burden, F. R.: Theoret. chim. Acta (Berl.) **12**, 95 (1968).
25. Levenberg, K.: Quart. Appl. Math. **2**, 164 (1944).
26. Papousek, D., Tolman, S., Pliva, J.: J. molecular Spectroscopy **15**, 502 (1965).
27. Arley, N., Buch, K. R.: Introduction to the theory of probability and statistics. New York: John Wiley and Sons 1953.
28. Golike, R. C., Mills, I. M., Person, W. B., Crawford, B., Jr.: J. chem. Physics **25**, 1266 (1956).
29. Duncan, J. L., McKean, D. C.: J. molecular Spectroscopy **27**, 117 (1968).
30. — Burns, G. R.: J. molecular Spectroscopy **30**, 253 (1969).

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