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The Absorption Spectra of Cyclopropane, Ethylene Oxide, Ethylene Sulfide, and Ethylene Imine in the Photographic Infra-Red*

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The absorption spectra of cyclopropane, ethylene oxide, ethylene sulfide, and ethylene imine have been investigated in the region between 7000 and 12,000 Å and the stronger bands have been assigned as third harmonics of the fundamental C—H stretching frequencies of these molecules. Rotational fine structure was not observed under high dispersion, but the well-defined band envelopes of the three asymmetric rotators provide interesting examples of these little investigated band types.

INTRODUCTION

ALTHOUGH the majority of compounds of chemical interest are asymmetric rotators, comparatively little is known about the types of band envelopes which may be expected in the absorption spectra of any molecules of large asymmetry. The only molecule of considerable asymmetry whose spectrum has been investigated in great detail is water. This is a spindle-shaped rotator, and unfortunately the simplicity of the molecule prevents the occurrence of one of the three elementary band types. Still less is known about the spectrum of the asymmetric disk-shaped molecule, and hence it has been thought of interest to investigate a number of disk-shaped molecules of considerable asymmetry, and of sufficient complexity to insure the appearance of all of the elementary band types. The ethylene oxide and ethylene sulfide molecules were chosen because their moments of inertia are not too large, and their C—H frequencies are high enough to bring their third harmonics well within the range of the present Eastman I-Z plates. Ethylene imine was included in order to observe the envelope of the hybrid third N—H harmonic. Cyclopropane, the related symmetric rotator, whose fundamentals have been carefully investigated, was also studied to assist in making the vibrational assignments.

EXPERIMENTAL

The cyclopropane employed in these experiments was a pure commercial product prepared

by the Ohio Chemical Company for use as an anaesthetic, and was used directly from the ampoule. Photographs were taken at pressures ranging from 120 mm to 1 atmosphere, the gas being confined in a 6-meter absorption tube.

Commercial ethylene oxide, obtained from the Ohio Chemical Company, was also used directly from the tank, photographs being taken at pressures ranging from 120 mm to 1.5 atmospheres in the 6-meter tube, and at a pressure of 1 atmosphere in the 72-foot absorption tube of this laboratory.

The ethylene sulfide was prepared from ethylene dithiocyanate kindly furnished by Dr. E. R. Buchman, according to the method of Delépine and Eschenbrenner.¹ The product was simply distilled, as it is decomposed by the ordinary drying agents, and photographed at a pressure of 200 mm in the 6-meter tube.

The ethylene imine sample was prepared from redistilled monoethanolamine by the method of Wenker,² and the product, twice distilled and dried over metallic sodium, was photographed at pressures ranging from 240 to 40 mm in the 6-meter tube. A second sample, kindly prepared by Mr. Herbert Sargent, Jr. according to the same method, was photographed at a pressure of 1 atmosphere in a 3-meter absorption tube.

Low dispersion spectrograms were first taken on a Bausch and Lomb glass Littrow spectrograph, and the strong bands were then photographed under the high dispersion of the 21-foot grating spectrograph.

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 659.

¹ Delépine and Eschenbrenner, *Bull. Soc. Chim. France*, **33**, 703 (1923).

² Wenker, *J. Am. Chem. Soc.* **57**, 2328 (1935).

VIBRATIONAL STRUCTURE

From the standpoint of their fundamental frequencies, the molecules cyclopropane, ethylene oxide and sulfide, and ethylene imine form an interesting sequence. The four C—H stretching frequencies π_s , $\pi_a(2)$, σ_s , $\sigma_a(2)$ of cyclopropane,³ go over to the four nondegenerate frequencies π_s , π_a , σ_s , σ_a of ethylene oxide as the symmetry is reduced from that of D_{3h} to C_{2v} , and the number of H atoms from six to four. In ethylene imine, which undoubtedly has the symmetry C_s , with the symmetry plane normal to the ring, the four C—H frequencies will remain rather similar to those of ethylene oxide, and may be characterized as π'_s , π'_a , σ'_s , σ'_a , where the π' and σ' indicate, respectively, symmetry and anti-symmetry with respect to the symmetry plane of the C_2H_4 group, normal to the actual plane of symmetry of the molecule. The N—H stretching frequency, which may be called simply s , will be symmetric with respect to the symmetry plane. Table I shows the distribution of these frequencies among the irreducible representations of the appropriate point groups, and the infra-red activities of their fundamentals. It should be noted that Table I defines the location of the z axis normal to the plane of the three-membered ring, and of the x and y axes in the plane of the ring, with the former passing through the hetero-atom. The selection rules for the third harmonics and combinations of these frequencies, which are of greatest importance in this region of the spectrum, may be obtained by the usual group-theoretical methods.⁴ This process yields the information that when only the above frequencies are considered, seven parallel and seven perpendicular bands are permitted for cyclo-

TABLE I. *Infra-red activity and irreducible representations of the high frequency fundamental modes of C_3H_6 , C_2H_4O , C_2H_4S , and C_2H_5N .*

$D_{3h}(C_3H_6)$	$C_{2v}(C_2H_4O, C_2H_4S)$	$C_s(C_2H_5N)$
$\pi_s, A'_1,$	π_s, A_1, M_x	π'_s, A', M_x, M_z
π_a, E', M_{\perp}	π_a, B_1, M_y	π'_a, A'', M_y
σ_s, A'_2, M_{11}	σ_s, B_2, M_z	σ'_s, A', M_x, M_z
$\sigma_a, E'',$	σ_a, A_2	σ'_a, A'', M_y
		s, A', M_x, M_z

³ See King, Armstrong, and Harris, J. Am. Chem. Soc. **58**, 1580 (1936) for diagrams of symmetry coordinates corresponding to these cyclopropane frequencies.

⁴ L. Tisza, Zeits. f. Physik **82**, 48 (1933).

TABLE II. *Observed bands, rotational structure types, and assignments.*

C_3H_6	C_2H_4O	C_2H_4S	C_2H_5N
	8333		
	8466		
	8602.1 A or C		
	8667.0 B, $3\pi_s$	8637 A, $3\pi_s$	8642.3 B, $3\pi'_s$
8691.4II	8767.3 C		
8770.5I, $3\pi_a$	8773.8 A, $3\pi_a$	8771.9 B, $3\pi_a$	8775.0 A, $3\pi'_a$
8806.0II	8815.8 B		
	8835.8 C	8833.8 C	
	8881.3 A	8909	8921
9006.8II		8982	
9114.4II, $3\sigma_s$	9021.7 C, $3\sigma_s$	9080.2 C, $3\sigma_s$	9065.3 C, $3\sigma'_s$
	9483		9552.5 $3s$
	9704		
	9807		
11448 complex	11333 complex	11413 complex	11390 complex
			12420 $4s$

propane in the third harmonic region, while for ethylene oxide and sulfide fifteen bands are permitted, five of each of the three types A , B , and C . In ethylene imine, no less than twenty bands are permitted. While many of these bands will, of course, not be strong enough to be observed, the spectra do prove to be so complex that assignments can be made in only a few cases. In Table II are listed the observed frequencies, as well as a correlation of bands which appear to be analogous, and assignments of the active third harmonics in the four compounds. Wherever possible, the probable rotational structure types, A , B , or C , whose identification will be discussed in more detail in the next section, have also been indicated.

BAND ENVELOPES

As might well be expected, none of the observed bands showed a resolvable rotational structure, but the unresolved band envelopes do possess considerable significance in themselves. The envelopes of symmetric rotator bands have been calculated theoretically by Gerhard and Dennison,⁵ and the observed cyclopropane bands seem in satisfactory agreement with the theory, though overlapping of the 8770 and 8806 cm^{-1} bands makes the interpretation of the microphotometer traces of the perpendicular band rather difficult. The envelopes of the asymmetric rotator bands, however, are of the greatest interest. When the normal modes of vibration of an asymmetric rotator are such that the changes of electric moment are along single principal

⁵ Gerhard and Dennison, Phys. Rev. **43**, 147 (1933).

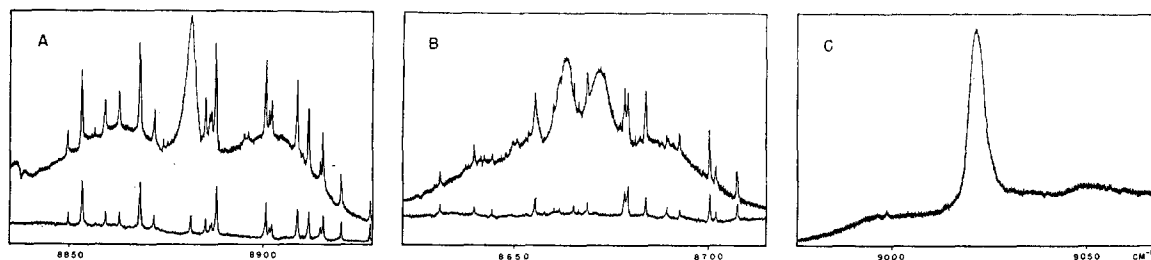


FIG. 1. Microphotometer traces of the three types of band envelopes of ethylene oxide. A trace of the water spectrum is included with the *A* and *B* type bands, which are contaminated with strong water lines.

axes of inertia of the molecule, the resulting rotational structures may be said to be of pure types, and are conveniently characterized as of types *A*, *B*, or *C*, as the change of electric moment is along the minor, intermediate, or major axis of the inertial ellipsoid. In molecules of symmetry C_1 , C_i , C_2 , or C_s , where the change of electric moment may have components along more than one axis, bands of a twofold (C_2 , C_s) or threefold (C_1 , C_i) hybrid type may appear, whose envelopes are linear combinations of the intensity distribution functions for the three related pure band types, with coefficients proportional to the squares of the components of the change of electric moment along the corresponding principal axes. In order to know which type of band should be associated with each of the C—H frequencies, it is necessary to know the location of the three different inertial axes in the molecule. For this purpose, approximate moments of inertia of ethylene oxide and ethylene sulfide were calculated on the basis of reasonable molecular models,⁶ giving the following values, in $\text{g cm}^2 \times 10^{-40}$:

Ethylene Oxide	Ethylene Sulfide
$I_y = A = 31.8$	$I_x = A = 38.8$
$I_x = B = 39.2$	$I_y = B = 74.8$
$I_z = C = 59.0$	$I_z = C = 102.0$

The moments of inertia of ethylene imine are very nearly equal to those of ethylene oxide. These results, in conjunction with Table I, make possible the following correlation between the band types and the irreducible representations of the normal modes:

Ethylene Oxide	$A \sim B_1$, $B \sim A_1$, $C \sim B_2$
Ethylene Sulfide	$A \sim A_1$, $B \sim B_1$, $C \sim B_2$
Ethylene Imine	$A \sim A''$, B , C hybrid $\sim A'$

⁶ Dr. H. A. Lévy has kindly informed me of preliminary results of his electron diffraction studies of the compounds.

The *A'* harmonics in ethylene imine may possess hybrid rotational structure, but this could hardly be observable for the C—H harmonics unless they also involve a considerable stretching of the N—H bond. The N—H bands, on the other hand, would be expected to present a twofold hybrid structure involving the band types *B* and *C*.

These predictions are confirmed in every respect by the observed band envelopes. The ethylene oxide bands at 8667, 8881, and 9022 cm^{-1} , shown in Fig. 1, are definitely of three different types, of which two are indeed somewhat similar in appearance but differ greatly in the relative intensities of the side and central branches. Since the 9022 cm^{-1} band appears to be the analogue of the 9114 cm^{-1} band of cyclopropane, one may with confidence identify the former as of type *C*. The 8667 cm^{-1} band, appears to be of type *B*, which will differ from the perpendicular band of the symmetric disk-shaped rotator principally in the appearance of a minimum of intensity at the origin. The remaining band at 8881 cm^{-1} may consequently be designated as type *A*. This identification may seem a little less arbitrary after the publication of theoretical calculations of the three types of band envelopes, which are now in progress in this laboratory. The C—H bands of ethylene imine showed no evidence of hybrid structure, and were very similar in appearance to the corresponding ethylene oxide bands. The type *C* band of ethylene sulfide showed scarcely a trace of side branches, and even when microphotometered seemed to be little more than a single intense central branch. The type *A* bands were weak, yet seemed rather similar in appearance to the type *A* bands of ethylene oxide. However, the type *B* band, shown in Fig. 2,

demonstrates in a very striking manner the effects of the change in the moments of inertia from those of ethylene oxide. The band is obviously considerably distorted as a result of the difference in the moments of inertia in the two vibrational states, but the important feature is that the double maxima about the band center have here become more widely separated, and much less intense relative to the rest of the band.

The ethylene imine band at 9553 cm^{-1} does indeed show the expected hybrid structure, as can be seen by comparing Fig. 3 with the corresponding pure band types, *B* and *C*, of ethylene oxide. The low frequency maximum seems a little too intense, but it may have been strengthened by an accidental superposition of a weak band of type *C*. This view is supported by the doubling observed in this maximum. The surprising feature of this band is the low intensity of the type *C* *Q* branch, which means that the contribution of the type *C* structure is very small. If it were feasible to determine intensities in this region, the contribution of the two components could be determined with some accuracy, since the intensity distribution functions for the two pure band types involved could then be determined experimentally from the C—H bands of the very similar ethylene oxide molecule. If it were then possible to be certain that the change of electric moment took place along the line of the N—H bond, the angle between this bond and the plane of the ring could be calculated. The problem is a complicated one, but it surely appears that this angle is much smaller than the

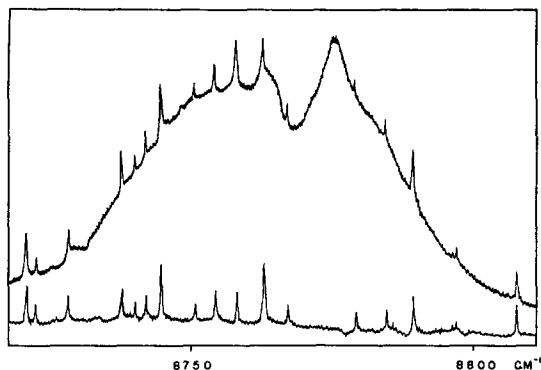


FIG. 2. Microphotometer trace of the strong type *B* band of ethylene sulfide. A trace of the water spectrum in this region is included.

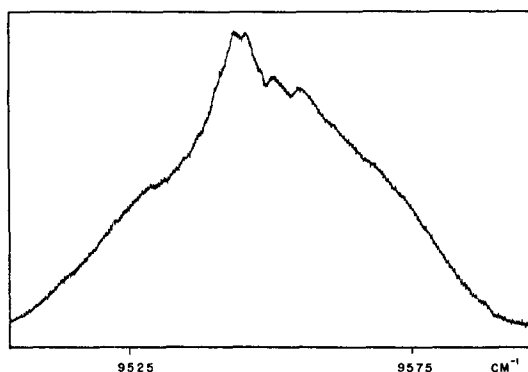


FIG. 3. Microphotometer trace of the hybrid N—H band of ethylene imine.

64° angle between one N—H bond in NH_3 and the plane of the other two bonds. The structure of N-methyl ethylene imine is being studied in these laboratories by Dr. H. A. Lévy, to see if the analogous angle in this compound can be determined with assurance.

It is of interest to observe that in all these molecules analogues of the 8720A (11465 cm^{-1}) band of ethylene⁷ appear with considerable intensity. These bands in cyclopropane and ethylene oxide were photographed under high dispersion, and in both cases were found to be unresolved bands of considerable complexity, apparently the result of the superposition of a number of simple bands. Definite assignments of the components is not possible, since even in cyclopropane, which has been most carefully studied, the assignments of the C—H bending frequencies does not seem completely satisfactory. It is, however, probable that in all cases these bands are the result of the superposition of combination bands involving three C—H stretching and two C—H bending frequencies.

The other bands of Table II were too weak for high dispersion study, and many were visible only on the low dispersion plates.

The author is glad, in conclusion, to express his appreciation to Dr. E. R. Buchman and Mr. Herbert Sargent, Jr., of these laboratories, for their advice and assistance in the preparation of ethylene imine and ethylene sulfide, and to Professor R. M. Badger for much helpful assistance throughout the course of these investigations.

⁷ Badger and Binder, Phys. Rev. **38**, 1442 (1931).