N72-28821

Infrared Spectra of Molecules and Materials of Astrophysical Interest

Grant NGR-41-002-033

Quarterly Progress Report

Report Number 19

March 1972

CASE FILE
COPY

Office of Grants and Research Contracts
Office of Space Science and Applications
National Aeronautics and Space Administration
Washington, D. C. 20546

(Prepared under Grant NGR-41-002-033 by the

University of South Carolina, Columbia, South Caroline 29208)

Principal Investigator - James R. Durig, Professor of Chemistry

Period Covered: 15 December 1971 to 15 March 1972

SUMMARY OF PROGRESS

Gerard P. Kuiper[1] has pointed out that the Jovian atmospheres are expected to contain H_2, He, N_2, H_2O, NH_3, CH_4, Ar and possibly SiH_4. He has also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below 120°C [see Table 8, pg. 349-350 of reference (1)]. He has also pointed out that until more is known about the atmospheres of the planets, it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work.

We have been studying the vibrational spectra from 4000 to 33 cm^{-1} of several molecules which may be present in the atmosphere of the Jovian planets. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the composition of the cloud covers of several of the planets; (2) provide structural information under favorable circumstances; (3) provide necessary data from which accurate thermodynamic data can be calculated; (4) and furnish information as to the nature of the potential energy function of the molecules and forces acting within them.

Some of the molecules which we have studied can be produced photochemically from methane, ammonia, and hydrogen sulfide which are thought to be constituents of the planets with reducing atmospheres. Some of the compounds will polymerize under ultraviolet radiation and drop out of the atmospheres. However, planets with a hot base, like that of Jupiter, may rebuild molecules destroyed photochemically. Therefore, we have used these criteria in selecting the compounds which we have studied. In our initial work on the vibrational spectra of molecules of astrophysical interest we studied hydrazine[2] and methylamine.[3] However, there are several other small molecules which contain hydrogen, carbon and nitrogen which also should be possible constituents of the recuding atmospheres, and we previously selected methylhydrazine[4], unsymmetrical dimethylhydrazine[5], symmetrical dimethylhydrazine[6], propylene imine[7], 1-pyrazoline[8], HNCS and DNCH[9], and dimethylaminodichlorophosphine[10]. In our continuing study of nitrogen containing compounds, we initiated a vibrational study of tetramethylhydrazine as well as the corresponding perfluoro compound.

Our results on the perfluoro molecule were communicated in the seventeenth progress report in December. The result of this study has also been accepted for publication in the journal of Inorganic Chemistry and the final results, essentially as they will appear in the journal,were included as appendix I in the eighteenth progress report. As also stated in this eighteenth progress report, we have been studying the vibrational spectra of tetramethylhydrazine, but we are still questioning the authenticity of at least three Raman lines. It is believed that these particular lines may result from a 2 to 5% impurity. We are currently purifying the sample with a low temperature fractionation column. This last experiment should complete our work on the tetramethylhydrazine molecule and we expect to have a paper ready for publication by the June progress report.

We have initiated vibrational studies on tetramethyltetrazine, $(CH_3)_2NNNN(CH_3)_2$. This molecule satisfies the above mentioned criteria. We have recorded the Raman and infrared spectra but no conclusions have been made at this time.

Closely related to these nitrogen containing compounds has been our work on the carbonyl containing molecules. We have previously reported work on carbon trioxid[11], trifluoromethyl peroxide[12], ethylene carbonate[13], γ-butyrolactone[13], cyclopentanone[13], oxalyl chloride[14], glyoxal[15], oxalyl bromide[16], oxalyl fluoride[17], 2,3-butanedione(biacetyl)[18], thiooxamide[19], and oxamide[19]. We have now concluded our work on the microwave spectrum of cis glyoxal.

It has been found that isomers resulting from rotation around the central C-C bond for several molecules of chemical formula $(COX)_2$, where X=F,Cl,Br,H and CH_3, exist in appreciable concentrations in the fluid states for the halogen-containing molecules. The vibrational data for the gas and liquid have been shown to be consistent with the trans form and a second isomer which has been assumed to be the cis form,although it is not possible to distinquish this structure from the gauche isomer from the observed vibrational spectra. In these studies it has been shown that structural conclusions can only be correctly made if the infrared and Raman spectra are obtained for these compounds in at least two different physical states with one of them being the solid. In our work on glyoxal, it was not possible to obtain the Raman spectrum of either the gas or liquid and no information on a second isomer could be obtained. However, Currie and Ramsay[20] recently reported an electronic band at 4875Å which was attributed to the cis form of glyoxal. They point out that the determined rotational constants should appreciably aid in the search for the microwave spectrum of this isomer. Therefore, we have recorded the microwave spectrum of glyoxal from 18.0 to 40.0 GHz at room temperature and the results are reported herein. Only B-type transitions were observed. Both Q-branch and R-branch assignments have been made for the ground and first three excited states of the internal rotational mode. From relative intensity measurements of vibrational excited states, the torsional vibration is found to have a frequency of 91±10 cm^{-1}. From a consideration of the rotational constants, it is concluded that the isomer giving rise to the microwave spectrum is the planar cis form and not the gauche isomer. The dipole moment was determined to be 4.66±0.02D. The results of this work are summarized in Appendix I.

It has been known for over 100 years that the Jovian cloud deck contains regions that are not neutral in tint. The Great Red Spot is the best known example, but there are other smaller features that exhibit various pastel colors. These color variations are especially interesting, because the known constituents of the atmosphere will not produce such effects by themselves. Unknown materials must be responsible for these large scale variations in tint and this is clearly an area of atmospheric chemistry that requires further investigation.

Various sources of coloration have been suggested. For example, Wildt[21] pointed out that a wide variety of colors can be produced by solutions of metallic sodium in ammonia but Urey[22] has objected to this interpretation on the grounds that it required a source of pure sodium in the planet's upper atmosphere. Urey[22] suggested the presence of organic polymers which could be formed by photochemical reactions from the atmosphere's basic constituents. This suggestion has received some support from recent laboratory experiments carried out by Woeller et al.[23] in which a mixture of methane and ammonia were subjected to an electrical discharge and a reddish polymer was formed. Another alternative proposed by Rice[24] suggested the coloration comes from free radicals which are frozen out in the clouds. For example, the radicals $(NH)_n$ and $(CH_3)_3CS$ appear blue and red, respectively. However, most of the substances suggested by Rice become unstable at temperatures above 115°K which is probably close to the tropopause temperature for Jupiter. The suggestion by Lewis[25] that the lower cloud deck might be composed of NH_4SH raises the possibility that yellow-brown $(NH_4)_2S$ may also be present[26]. Thus, there is a large diversity of opinion as to the most significant contribution to the observed coloration.

If Urey's interpretation[22] is correct, then it may have pronounced consequences from the standpoint of the theories of the origin of life. It has been suggested that the organic molecules required for the development of life on the earth were produced at a time when our atmosphere contained a large amount of ammonia and methane. Thus, the present composition of the lower atmosphere of Jupiter is probably not fundamentally very different from primitive earch as stressed by Sagan[27]. One is thus confronted with the possibility that the same essential pre-life chemical reactions that occured on the earth are at present taking place on Jupiter[28].

If this picture of the Jupiter atmosphere is correct, then why have none of these organic molecules been identified? Owen[28] has pointed out that only the ultraviolet and infrared region of the spectrum can be used for identification purposes and the critical region of the u.v. below 3000 Å has been inaccessible to observation. Also the infrared region is badly cut by strong ammonia and methane absorptions. Finally, if these substances are present in the cloud particles, then the scientist will be dealing with reflection spectra of solids which Owen states to be "notoriously difficult to interpret". <u>Thus we are continuing our research on the vibrational spectra of molecular crystals</u>. We believe in the past year that we have shown that the infrared spectra of molecular solids are no more difficult to interpret than the normal infrared spectra and that Owen is essentially incorrect on this point. However, more data are certainly needed on molecular crystals so it will be available when better infrared data is obtained for Jupiter.
Owen stated that the lower levels of the atmosphere probed in the infrared may offer the best hunting ground for the identification of these organic sub stituents of the Jovian atmosphere and we are in complete agreement. Therefore,

we have completed the vibrational studies on solid acetaldehyde and acetaldehyde-d_4 and report the results herein.

Previously, a number of molecules with a single methyl rotor were examined to determine the effect of phase changes on the barrier to internal rotation[29]. Included in this study were a number of ethane derivatives - ethyl and acetyl halides. It was found that the barrier height increased on going from the gas phase to the solid phase by approximately 15%. The barrier heights were approximately the same (4.5 kcal/mole) for the three ethyl halides (Cl, Br, I), and the two acetyl halides, CH_3CClO and CH_3CBrO, revealed considerably lower barriers (1.9 kcal/mole) than their ethyl halide counterparts in the solid. To continue the study on the effects of phase changes upon torsional barriers and the determination of the frequencies of the lattice modes of molecular crystals, we have initiated a study of the far infrared and Raman spectra of solid CH_3CHO and its deuterated analogue.

Vibrational assignments for the intramolecular fundamentals, except for the torsion have been published by a number of authors[30-38]. In the most recent and also the most complete study, Hollenstein and Günthard[38] assigned the torsional mode from combination bands in the mid-infrared spectra of both the solid and gas. Their assignment for the gas was in agreement with that previously proposed by Winther and Hummel[39]. Direct observation of the torsional mode in the far infrared spectrum of the gas has also been reported[40-42] with the data of Souter and Wood being consistent with the barrier obtained from microwave studies[38,42-44]. In an earlier study, Möller had reported[40] a torsional frequency of 175 cm^{-1} which was at variance with the most recent work, so we have re-investigated the far infrared spectrum of the gas in order to determine the origin of this discrepancy.

The results of this study are summarized by the following abstract of the paper submitted for publication of this work:

ABSTRACT: The far infrared (550-33 cm^{-1}) and Raman (300-0 cm^{-1}) spectra of solid CH_3CHO and CD_3CDO have been recorded. The torsion appears in the solid phase spectra of both techniques at approximately 205 cm^{-1} ($V_3 = 2.10$ kcal). Compared to the infrared data, the Raman data obtained and reported here was found to be far superior, and eighteen of the twenty-one predicted intermolecular fundamentals were resolved in the Raman spectrum of solid acetaldehyde. Out of the nine predicted translations, seven could be confidently assigned and at least nine of the twelve predicted librations were observed.

The results of this study are included as Appendix II of this report.

Future Work (NGL-41-002-033)

We are continuing our investigation of the vibrational spectra of small molecules which may be possible constituents of the Jovian atmospheres. The data will be used to calculate thermodynamic properties, force constants, and other useful molecular properties when possible. At present, we are finishing the work on the tetramethylhydrazine. Also, we have nearly completed a microwave investigation of γ-butyrolactone and it appears that at room temperature that the molecule has a relativly large barrier to pseudorotation. Work is near completion on dimethylamine and dimethylphosphine, both of which fits the criteria as possible constituents of the Jovian atmospheres. We have also initiated studies on nitric oxide dimer (N_2O_2). Our results for these latter molecules will be reported in the next progress report. We are continuing our work on the vibrational spectra of molecular crystals.

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APPENDIX I

MICROWAVE SPECTRUM OF CIS GLYOXAL

ABSTRACT: The rotational spectrum of glyoxal has been investigated in the region 18.0 - 40.0 GHz. Only B-type transitions were observed. Both Q-branch and R-branch assignments have been made for the ground and first three excited states of the internal rotational mode. From relative intensity measurements of vibrational excited states, the torsional vibration is found to have a frequency of 91±10 cm^{-1}. From a consideration of the rotational constants, it is concluded that the isomer giving rise to the microwave spectrum is the planar _cis_ form and and not the _gauche_ isomer. The dipole moment was determined to be 4.66±0.02D.

Recently, we have recorded[1-4] the vibrational spectra of several molecules of chemical formula $(COX)_2$, where X = F,Cl,Br,H and CH_3 and determined their molecular symmetries in the solid and fluid states. It has been found that isomers resulting from rotation around the central C-C bond exist in appreciable concentrations in the fluid states for the halogen-containing molecules. The vibrational data for the gas and liquid have been shown to be consistent with the trans form and a second isomer which has been assumed to be the cis form although it is not possible to distinguish this structure from the gauche isomer from the observed vibrational spectra. In these studies it has been shown that structural conclusions can only be correctly made if the infrared and Raman spectra are obtained for these compounds in at least two different physical states with one of them being the solid. In our work on glyoxal, it was not possible to obtain the Raman spectrum of either the gas or liquid and no information on a second isomer could be obtained. However, Currie and Ramsay[5] recently reported an electronic band at 4875Å which was attributed to the cis form of glyoxal. They point out that the determined rotational constants should appreciably aid in the search for the microwave spectrum of this isomer. Therefore, we have recorded the microwave spectrum of glyoxal from 18.0 to 40.0 GHz at room temperature and the results are reported herein.

EXPERIMENTAL

Glyoxal was obtained from K and K Laboratories, Inc., as a powdered trimer of 76% purity. The glyoxal monomer was obtained by heating the trimer under vacuum. The gas was passed over phosphorus(V)oxide and collected in a flask cooled by a dry ice-acetone bath. While still being cooled, the freshly collected solid was pumped on to remove any possible decomposition products. There appeared to be no appreciable polymerization of the solid, so long as it was kept at -78°C.

However, the microwave spectrum always contained extraneous lines which had varying intensity depending on the sample.

The microwave spectrum was recorded from 18.0 - 40.0 GHz on a Hewlett Packard Model 8460A MRR spectrometer with a stark cell modulation frequency of 33.3 kc/sec. All frequencies were measured at room temperature and the accuracy was estimated to be better than ±0.1 MHz.

SPECTRAL RESULTS

As a preliminary starting point, the microwave spectrum was calculated from the rotational constants published from the electronic study[5]. The Q-branch lines were readily identified by their fast Stark effects and their close proximity to the frequency values calculated. A Q-branch plot was made which is shown in Fig. I. In addition to the ground state transitions, three vibrational excited state transitions were also observed. Correct assignment was again verified by a Q-branch plot for the first excited state (see Fig. I). The R-branch transitions were then calculated from both the rotational constants from the electronic study and by the κ obtained from the Q-branch plot and an assumed inertial defect $\Delta=0$. From the expected intensities and the limited frequency range, there were only four sets of transitions and only one of these sets was consistent with the least squares fit of the rotational constants.

The assignment of the observed lines and their frequencies are listed in Table I along with the rotational constants calculated from the rigid rotor fit. The observed frequencies were found in reasonably good accordance with the predictions. Further confirmation of the assignment was made from the number and relative intensity of the Stark lobes.

Fig. 2 shows the Stark effect of the $3_{12}\leftarrow 3_{03}$ transition at two different voltages. The trace in Fig. 2-b was observed at a higher electric field than in Fig. 2-a. It is easily seen that these two Stark lopes must belong to $|M| = 2$ and $|M| = 3$ components. Their relative intensities are just what one expects for the 3←3 transition. Both components are moving to the higher frequency side with increasing electric field. We have carried out Stark effect measurements for $|M| = 1$ of the $1_{10}\leftarrow 1_{01}$ transition. Electric field calibration was made based on a moment of 0.71521D for OCS[6].

Because of the molecular symmetry, the dipole components μ_a and μ_c were assumed to be zero in the calculation. Interestingly enough, the dipole moment obtained ($\mu = 4.8\pm0.2$D) was formed to be about twice the dipole moment of HCHO[7].

DISCUSSION

Depending upon the relative positions of the two aldehyde groups rotating internally along the C-C bond, there are three possible rotamers for glyoxal, i.e. the <u>trans</u>, <u>cis</u> and <u>gauche</u> forms. The vibrational assignments for <u>trans</u>, glyoxal have been made by Harris[8] who observed the torsional frequency at 128 cm^{-1} from the sum and difference bands with the symmetric C-H and C=O stretches. The energy difference between the <u>cis</u>-form and the <u>trans</u>-form was reported by Currie and Ramsay[5] to be 1125±100 cm^{-1} in favor of the latter. By using these two experimental pieces of information, it is possible to derive the torsional potential function of the form, $V = 1/2 \sum_{n=1}^{2} V(1-\cos n\phi)$, as long as the molecular structure is known.

The molecular structure of <u>trans</u> glyoxal has been determined to be: r(C-C) = 1.526A, r(C=O) = 1.212A, r(C-H) = 112.2Å, ∢CCO = 121.2° and ∢CCH = 112.2° by Kuchitsu, Fukuyama and Morino[9] using the electron diffraction method. The F value, which is related to the reduced moment of inertia I_r for the torsional motion about the C-C bond by $F(\mathrm{cm}^{-1}) = 16.857/I_r$, is calculated to be 3.38 cm^{-1} from the determined structure according to Pitzer's method[10]. Using the above potential form and by assuming the harmonic potential behavior around the equilibrium position of the *trans* form, we obtained the relationship between the torsional frequency(ν_t) in the *trans* form and the potential function coefficients to be $V_{1/2} + 2V_2 = V_t^2/2F$ where V_1 represents directly the energy difference between the *trans* and the *cis* forms. Thus, we obtained $V_1 = 1125\ \mathrm{cm}^{-1}$ and $V_2 = 930\ \mathrm{cm}^{-1}$. This potential function has the form shown in Fig. 3.

Our experimental rotational constants give a small value of the inertia defect (see Table I) which suggests a planar structure for this molecule[11]. We can, therefore, conclude that the rotational transitions reported herein are due to the *cis* coplanar rotamer instead of the *gauche* form. Since the torsional mode in *cis* glyoxal is expected to have the lowest vibrational frequency, it is consistent to assign the strongest excited state line as arising from the molecules in the first excited torsional state. This assignment makes it possible to obtain the $1 \leftarrow 0$ torsional frequency for the *cis* form from the relative intensity measurements if there are no other interferences from other excited states to these two rotational lines.

In order to make a simple comparison of our relative intensity result with the torsional frequency calculated from the potential function around the *cis* position, we have to calculate the F value in the equilibrium position for the *cis* form. A rotation of 180 degrees from the *trans* position does not produce rotational constants close to the observed experimental values if the same structure parameters as in the *trans* form are assumed. Consequently, we have tried to adjust the C-C bond distance and CCO angle to give the best least square fitting to the experimental rotational constants under the assumption that the remaining parameters are identical with those for the trans form. Our results are: r(C-C) = 1.505 and ∢CCO = 123.9°. This new structure yields an F = 5.06 and predicts a torsional frequency of 107 cm^{-1} for the 1←0 torsional transition in the cis form. This frequency is in good agreement with the result of our intensity measurements (r_{exp} = 95±20 cm^{-1}).

In the Fourier expansion of the potential function governing the torsional motion, the small V_3 term has been judged negligible in the earlier vibrational work[a12]. The agreement of the measured frequency in the cis form with the calculated value from the two-term-potential function gives further support to the earlier judgement about neglecting the V_3 term. We did not use the present experimental data to include one more Fourier term in elucidating the potential function because of the large experimental error involved in measuring the torsional frequency for the cis form.

ACKNOWLEDGEMENTS

The authors should like to acknowledge the financial support given this work by the National Aeronautics and Space Administration by Grant NGR-41-002-003.

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Table I. Microwave Spectrum and Rotational Constants of cis Glyoxal in the Ground and Vibrationally Excited States (MHz and amu-Å^2).

Transition	Ground State Obs.	Obs.-Calc.	$\nu_\tau=1$	$\nu_\tau=2$
$1_{10} \leftarrow 1_{01}$	21680.68			
$2_{11} \leftarrow 2_{02}$	22886.86	-0.04		
$3_{12} \leftarrow 3_{03}$	24783.95	0.14	24871	
$4_{13} \leftarrow 4_{04}$	27472.50	-0.28	27642	
$5_{14} \leftarrow 5_{05}$	31076.20	0.13	31360	
$4_{04} \leftarrow 3_{13}$	26667.21	-0.22	26696	
$5_{05} \leftarrow 4_{14}$	39389.97	0.17	39465	

$A = 26723.86 \pm 0.28$

$B = 6200.97 \pm 0.03$

$C = 5042.79 \pm 0.06$

$K = -0.89316$

$I_a = 18.9111$

$I_b = 81.4996$

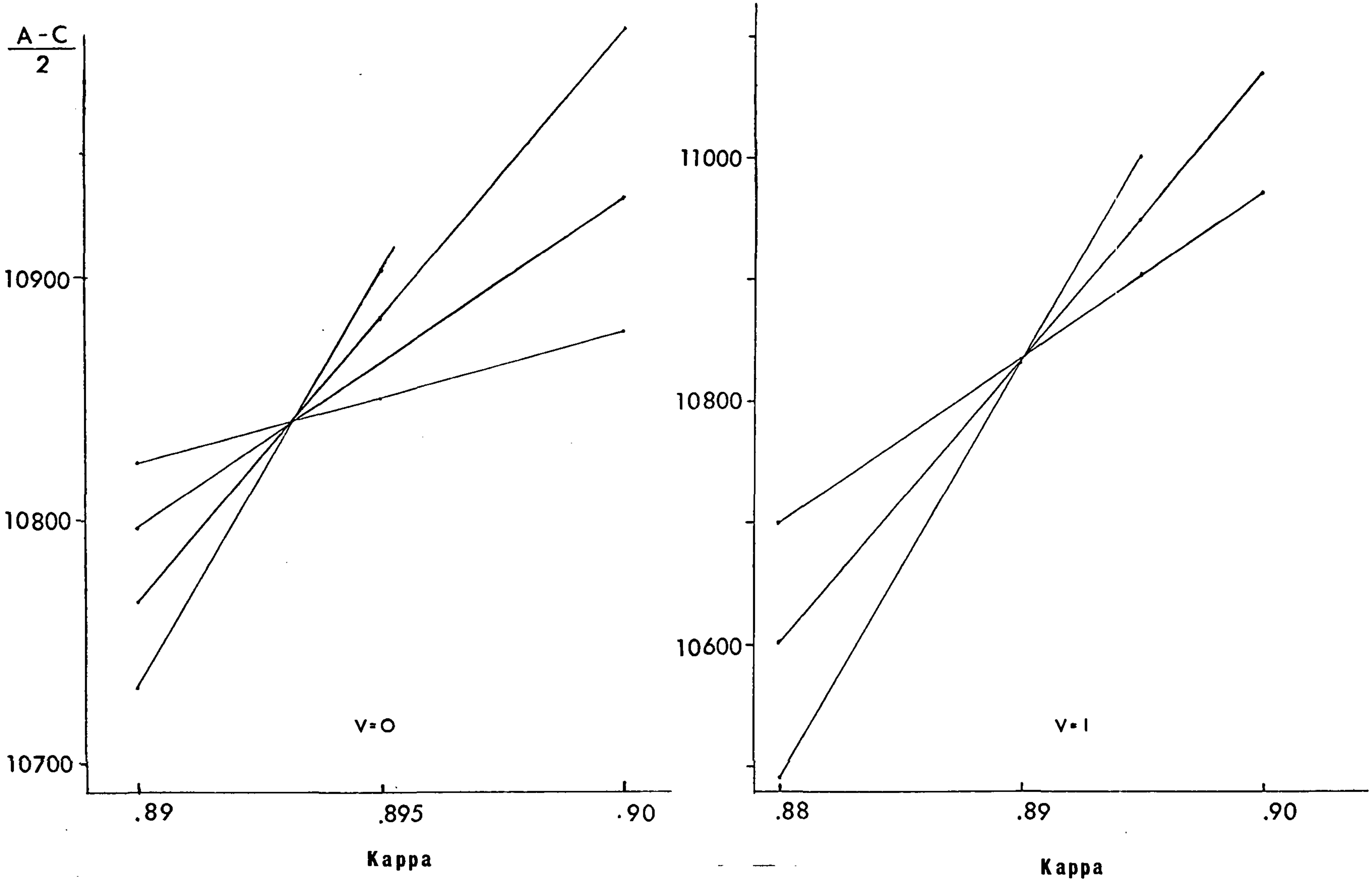
$I_c = 100.218$

$\Delta = 0.193$

FIGURE CAPTIONS

Fig. I Q-branch plot for the ground and first excited torsion state.

Fig. 2 The Stark effect of the $3_{12} \leftarrow 3_{03}$ transition at two different voltages.


$\frac{A-C}{2}$
10900
10800
10700
.89
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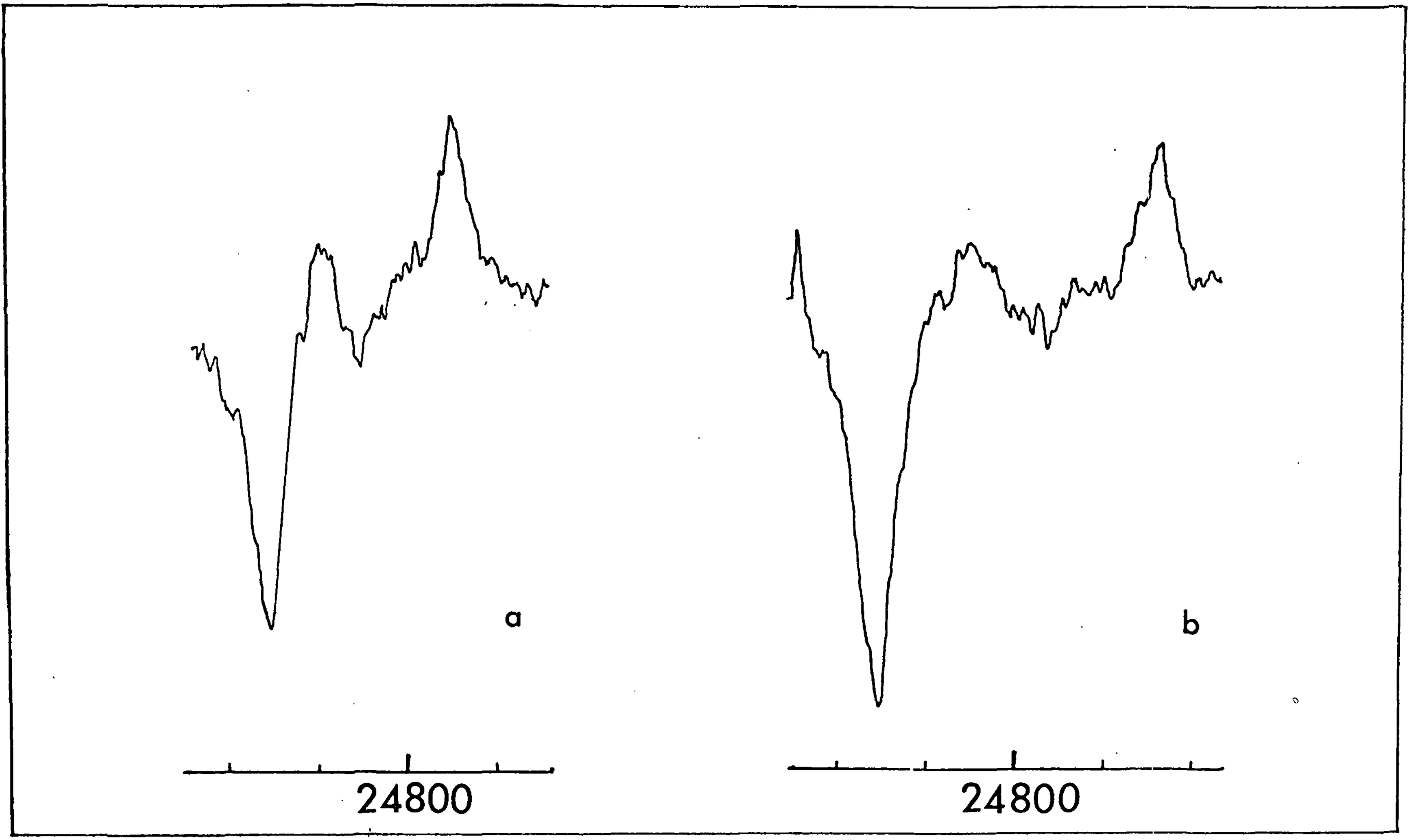
.90
Kappa
V=O
11000
10800
10600
.88
.89
.90
Kappa
V=1



MC/S

APPENDIX II

LOW-FREQUENCY MODES OF MOLECULAR CRYSTALS. XVIII†

ACETALDEHYDE AND ACETALDEHYDE-d_4

ABSTRACT: The far infrared (550-33 cm^{-1}) and Raman (300-0 cm^{-1}) spectra of solid CH_3CHO and CD_3CDO have been recorded. The torsion appears in the solid phase spectra of both techniques at approximately 205 cm^{-1} (V_3 = 2.10 kcal). Compared to the infrared data, the Raman data obtained and reported here was found to be far superior, and eighteen of the twenty-one predicted intermolecular fundamentals were resolved in the Raman spectrum of solid acetaldehyde. Out of the nine predicted translations, seven could be confidently assigned and at least nine of the twelve predicted librations were observed.

INTRODUCTION

Previously, a number of molecules with a single methyl rotor were examined to determine the effect of phase changes on the barrier to internal rotation[1]. Included in this study were a number of ethane derivatives - ethyl and acetyl halides. It was found that the barrier height increased on going from the gas phase to the solid phase by approximately 15%. The barrier heights were approximately the same (4.5 kcal/mole) for the three ethyl halides (Cl, Br, I), and the two acetyl halides, CH_3CClO and CH_3CBrO, revealed considerably lower barriers (1.9 kcal/mole) than their ethyl halide counterparts in the solid. To continue the study on the effects of phase changes upon torsional barriers and the determination of the frequencies of the lattice modes of molecular crystals, we have initiated a study of the far infrared and Raman spectra of solid CH_3CHO and its deuterated analogue.

Vibrational assignments for the intramolecular fundamentals, except for the torsion have been published by a number of authors [2-10]. In the most recent and also the most complete study, Hollenstein and Günthard [10] assigned the torsional mode from combination bands in the mid-infrared spectra of both the solid and gas. Their assignment for the gas was in agreement with that previously proposed by Winther and Hummel [11]. Direct observation of the torsional mode in the far infrared spectrum of the gas has also been reported [12-14] with the data of Souter and Wood being consistent with the barrier obtained from microwave studies [10, 14-16]. In an earlier study [12] Möller had reported a torsional frequency of 175 cm^{-1} which was at variance with the most recent work, so we have re-investigated the far infrared-spectrum of the gas in order to determine the origin of this discrepancy.

EXPERIMENTAL

Acetaldehyde samples were obtained from Eastman Kodak and K and K Laboratories and kept free from air between usage in evacuated vessels. Deuterated acetaldehyde, CD_3CDO, was purchased from Merck, Sharp and Dohme, with a stated purity of 99.5% and it was used without further purification.

Infrared spectra were recorded between 600 and 33 cm^{-1} on a Beckman IR-11. Water vapor was removed from the instrument housing by purging with dry air. The instrument was calibrated against the spectrum of atmospheric water by using the assignments of Hall and Dowling [17,18]. Spectra of polycrystalline samples were obtained by depositing, in vacuum, thin films onto a silicon plate cooled by boiling nitrogen. Spectra of the vapors were obtained from samples contained in a Beckman 10-meter variable path-length gas cell equipped with polyethylene windows.

Raman spectra were recorded with a Cary Model 82 spectrophotometer equipped with an argon-ion laser by using the 5145Å green line for excitation. The instrument was calibrated with neon emmission lines. A jacketed cold cell, in which a capillary could be inserted was used to obtain the Raman spectra of the solids. Variable temperatures ranging from -195°C to ambient, could be obtained by allowing cold nitrogen to flow through the cell around the capillary. Temperatures were measured with a thermocouple inserted in the refrigerant stream.

RESULTS AND DISCUSSION

The far infrared spectra of CH_3CHO and CD_3CDO are shown in Figs. 1 and 2, respectively. For the "light" molecule, there are five rather broad bands observed, whereas only four are observed for the deuterium compound. The frequencies of the observed bands are listed in Table 1 and the apparent shift factors appear confusing at first, particularly, for the two broad bands between 100 and 135 cm^{-1}. The determination of the band center for these two broad bands was quite difficult because of the breadth of the bands. Also, it is quite clear that these bands originate from intermolecular motions so the frequencies are dependent on the sample temperature and the crystallinity of the samples. To minimize these effects, the samples were always annealed until no further changes were noted in the frequencies or band contours. All samples were annealed to about -140°C; the spectra were then obtained with the sample temperature maintained as close to -190°C as possible. Nevertheless, differences of 3 or 4 cm^{-1} in band centers were observed for successive recordings of the same sample.

Inspection of the Raman data shown in Figs. 3 and 4 reveals a much better definition of the "individual" lattice modes. For example, the broad band at 128 cm^{-1} in the infrared spectrum of the "light" compound is clearly resolved into four definite lines in the Raman effect. Thus, consistent shift factors were obtained from the Raman data for the lattice modes of the two isotopic species. The base line was quite flat down to 15 cm^{-1} and a lattice mode was clearly detected at 20 cm^{-1} in both Raman spectra. Most of the low frequency Raman lines were quite sharp and their centers could be accurately measured. However, the expected shift factors with deuteration are quite small.

Methyl torsion --- An inspection of both the infrared and Raman spectra of the "light" molecule above 200 cm^{-1} compared to the corresponding spectra in the same region of the deuterated molecule shows the complete disappearance of the band(s) in this region. It either shifts to the low frequency side of the 170 cm^{-1} line or the high frequency side of the 127 cm^{-1} line. Since the latter shift factor is larger than the theoretical one calculated for the torsional motion or any of the librational motions, it seems reasonable to assign the 159 cm^{-1} shoulder in the spectrum of the deuterated molecule as arising from the same motion that leads to the 201 cm^{-1} line in the light molecule. Thus the 207 cm^{-1} line and 201 cm^{-1} shoulder in the Raman spectrum are assigned as the methyl torsional modes. The two bands are attributed to correlation field splitting in the crystal (see next section), which results from four molecules in the unit cell. This assignment agrees well with the 204 cm^{-1} prediction made by Hollenstein and Günthard [10] for the torsional mode in the solid state from the assignment of combination bands.

As pointed out in the introduction, Möeller [12] assigned the torsion to a strong band at 175 cm^{-1} in the infrared spectra of the gas phase. We have also been able to observe this band as well as a strong band at 270 cm^{-1} but only after the sample has been exposed for a period of time to the air. Freshly purified material did not show these two bands. Fateley and Miller [13] also had noted the absence of the 175 cm^{-1} band in their study of the infrared spectrum of the gas; however, they did report six weak absorption bands around 270 cm^{-1} in addition to the torsional mode which they assigned as being centered at 150 cm^{-1}. This assignment has also been used in the normal coordinate calculations of acetaldehyde [10,19]. Souter and Wood recently reported the far infrared results on gaseous CH_3CHO and CD_3CHO and they assigned the torsional mode for the "light" molecule at 143 cm^{-1} and attributed the peak at 150 cm^{-1} in the spectrum taken by Fateley and Miller to imperfect drying of the sample [14]. Our gas phase results for the "light" compound are consistent with those published by Souter and Wood. Thus the methyl torsional mode shifts from 143 to 204 cm^{-1} (average of 207 and 201 cm^{-1} lines) with solidification. This is one of the largest shifts observed for a methyl torsional mode in going from the gas to the solid state.

In order to obtain the barriers to internal rotation from the observed torsional frequencies in the gas and solid phases the F value (reduced moment parameter) must be determined from the structural parameters of the molecule. The values reported from Wilson's microwave analysis were used for the gas phase [15]. For the crystalline state we used the band distances reported by A. J. Richard [20]; however, since the geometry of the methyl group is not known with any certainty in the solid, a tetrahedral orientation of the C-H bonds and a C-H bond distance of 1.08Å was assumed. The difference between the F values obtained from the two phases (See Table II) may be seen to reflect the structural distortion of the free molecule upon crystallization.

Condensation of acetaldehyde results in an approximate one kcal/mole increase in the torsional barrier. The increase is considerably larger than those observed for the acetyl halides which are enumerated in Table III. The large difference probably results from the intermolecular potentials for acetaldehyde more nearly approximating the intramolecular potential for the methyl torsion than it does for the acetyl halides.

Intermolecular fundamentals --- A. J. Richard has found the crystalline structure of CH_3CHO to be $C_{2v}^{9}(P_{na}2_1)$ with the molecules occupying C_1 sites and four molecules per unit cell[20]. From the group theoretical considerations of Halford[27] and Hornig[28] one can predict the following representations for the lattice modes of CH_3CHO:

$$\Gamma = A_1(6) + A_2(6) + B_1(6) + B_2(6)$$

The acoustical translations fall into the species:

$$\Gamma(AT) = A_1 + B_1 + B_2$$

Thus, 21 spectroscopically active lattice modes are expected. The representations for the optical translations and librations are then:

$$\Gamma(OT) = 2A_1,(IR,R) + 3A_2(R) + 2B_1(IR,R) + 2B_2(IR,R)$$

$$\Gamma(OL) = 3A_1,(IR,R) + 3A_2(R) + 3B_1(IR,R) + 3B_2(IR,R)$$

Table IV gives the factor group analysis of acetaldehyde.

Theoretically, the intermolecular fundamentals may be distinguished by analyzing the observed frequency shift of a motion upon deuteration of the molecule. The shift factor for a translation upon deuteration of acetaldehyde should be proportional to the square root of the mass of CD_3CDO to that of CH_3CHO, or 1.04. Similarly, those shift factors associated with the librations depend upon the moments of inertia around the three principle axes of a molecule and its isomer. The principle moments of inertia for acetaldehyde were determined using the structure for the solid. Therefore, the theoretical shift factor for a libration which occurs about the "a" principle axis of acetaldehyde is 1.11, while it is calculated to be 1.10 and 1.24 for a libration about the "b" and "c" axes, respectively. The shift factors obtained experimentally are usually much smaller than the predicted values due to the large amount of anharmonicity associated with the intermolecular fundamentals.

From the Raman spectra of CH_3CHO and CD_3CDO_3 in figures 3 and 4, eighteen of the twenty-one predicted intermolecular fundamentals are readily observed. Because of the great similarity between the two spectra, all corresponding bands were easily identified. In fact, the effect of deuteration on the spectrum of acetaldehyde appears to be the shifting of the whole center portion of the spectrum a bit closer to the exciting line. Within this center region only one band apparently does not shift. From the band contours of the 117 cm^{-1} and 113 cm^{-1} bands in acetaldehyde, it is believed that the 117 cm^{-1} band shifted to the sharp 103 cm^{-1} band in deuterated acetaldehyde, whereas the broader 113 cm^{-1} band does not shift upon deuteration of the molecule. In Table V are listed the Raman frequencies observed and the corresponding shift factors obtained for the solid acetaldehyde isomers.

Those bands observed with a shift factor of one may be assigned to the translational motions of the lattice. Nine optical translations are predicted in the Raman effect and there are nine band assignments reported with a shift factor of one. However, translations are usually weak and the assignment of the strong bands 166 cm^{-1} and 45 cm^{-1} to translations must be considered tentative.

Librations about the "a" or "b" principle axes of acetaldehyde in the lattice are clearly not distinguishable from the shift factor data; however, those librations about the "c" principle moment should exhibit the largest shift factor for an intermolecular fundamental. The bands associated with the 1.11 and 1.09 shift factors may then be assigned to this libration. As a result of these assignments, seven of the nine translations may be confidently reported. Also at least nine of the twelve librations are reported where two of the bands observed may be assigned to a libration about the "c" axis of the molecule in the crystal.

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Table I. Low Frequency (cm^{-1}) Infrared Modes of Acetaldehyde

CH_3CHO (gas)	CH_3CHO (solid)	CD_3CDO (gas)	CD_3CDO (solid)
507	520	446	454
	207		
	169		170
	128		134
	103		110 103 shoulder
	81		81

Table II. Barriers to Internal Rotation of Acetaldehyde

	CH_3CHO		CD_3CDO	
State	Gas	Solid	Gas	Solid
F Value	7.93	7.69	4.53	4.45
Torsional frequency	143	204	116	162
Barrier (Kcal)	1.05	2.10	1.13	2.02

Table III. Three-fold Barriers to Internal Rotation

Compound	Barrier Height (V_3) Kcal/mole	Method	State	Reference
CH_3CHO	1.048	IR	gas	14
	2.108	IR	solid	this work
CD_3CDO	1.134	IR	gas	21
	2.068	IR	solid	this work
CH_3CFO	1.041	MW	gas	22
CH_3CClO	1.3	MW	gas	23
	1.85	IR	solid	24
CH_3CBrO	1.3	MW	gas	25
	1.97	IR	solid	24
CH_3CIO	1.3	MW	gas	26

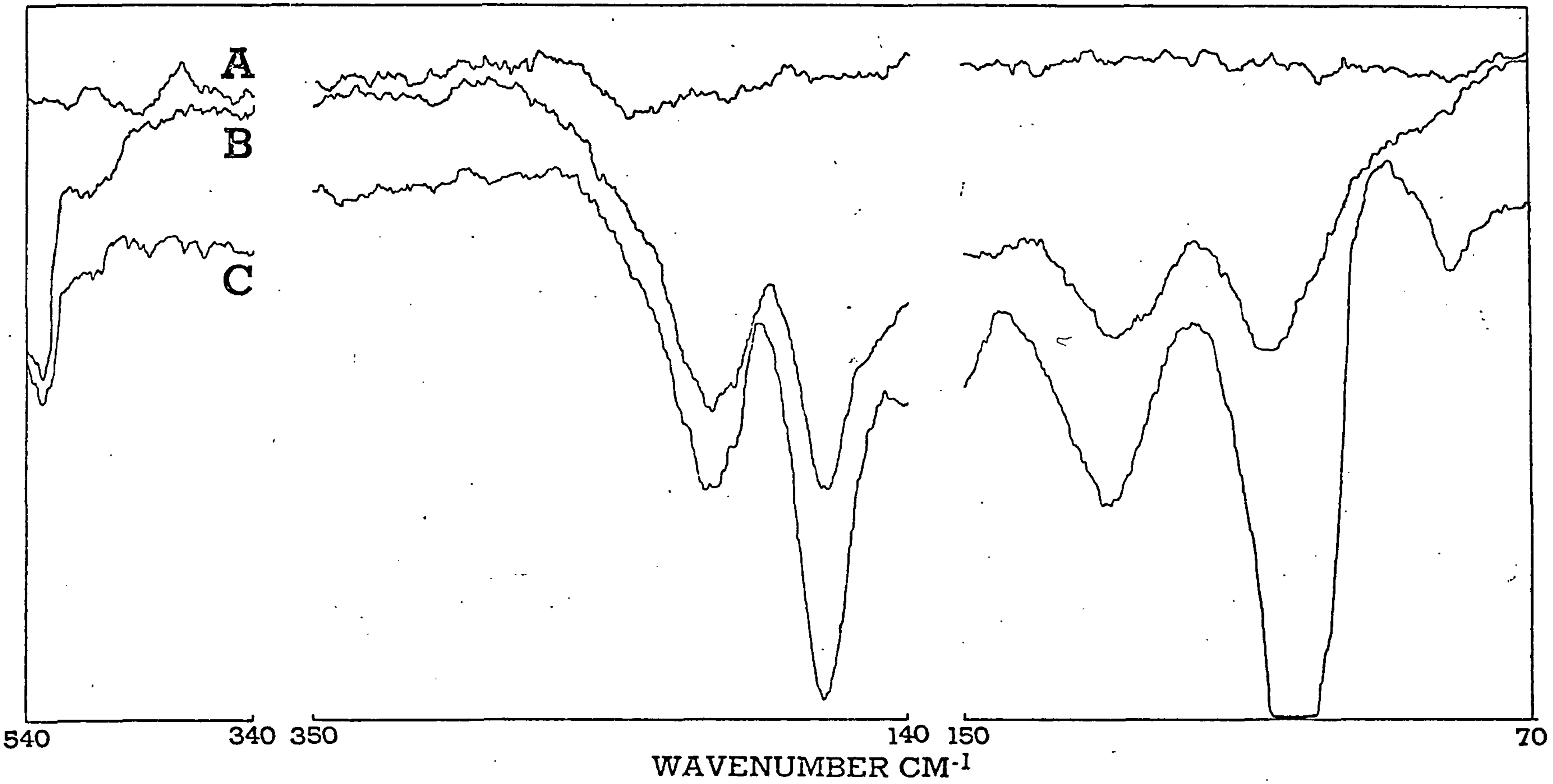
Table IV. Factor Group Analysis of Crystalline CH_3CHO

Molecule		Site	Factor	
C_s		C_1	$C_{2v}^{9} = P_{na}{}^{2}{}_{1}$	
			a_1	Z
R_z, X, Y	a'			
			a_2	R_z
		a		
			b_1	X,R_y
Z, R_x, R_y	a"			
			b_2	Y,R_x

Table V. Low Frequency Raman Modes of Acetaldehyde

CH_3CHO (solid)	CD_3CDO (solid)	Shift Factor
207	165.5	1.24
201	159.5	1.25
166	166.5	1
137	131	1.04
133	127.5	1.04
123	121.5	1.01
117	103	1.09
113	112.5	1
95	92	1.03
86.5	77.5	1.11
77.5	73	1.05
71	68.5	1.03
66	66	1
60	60	1
52	52	1
47	45	1.04
44.5	45	1
36	36	1
28	28	1
20	20	1

List of Figures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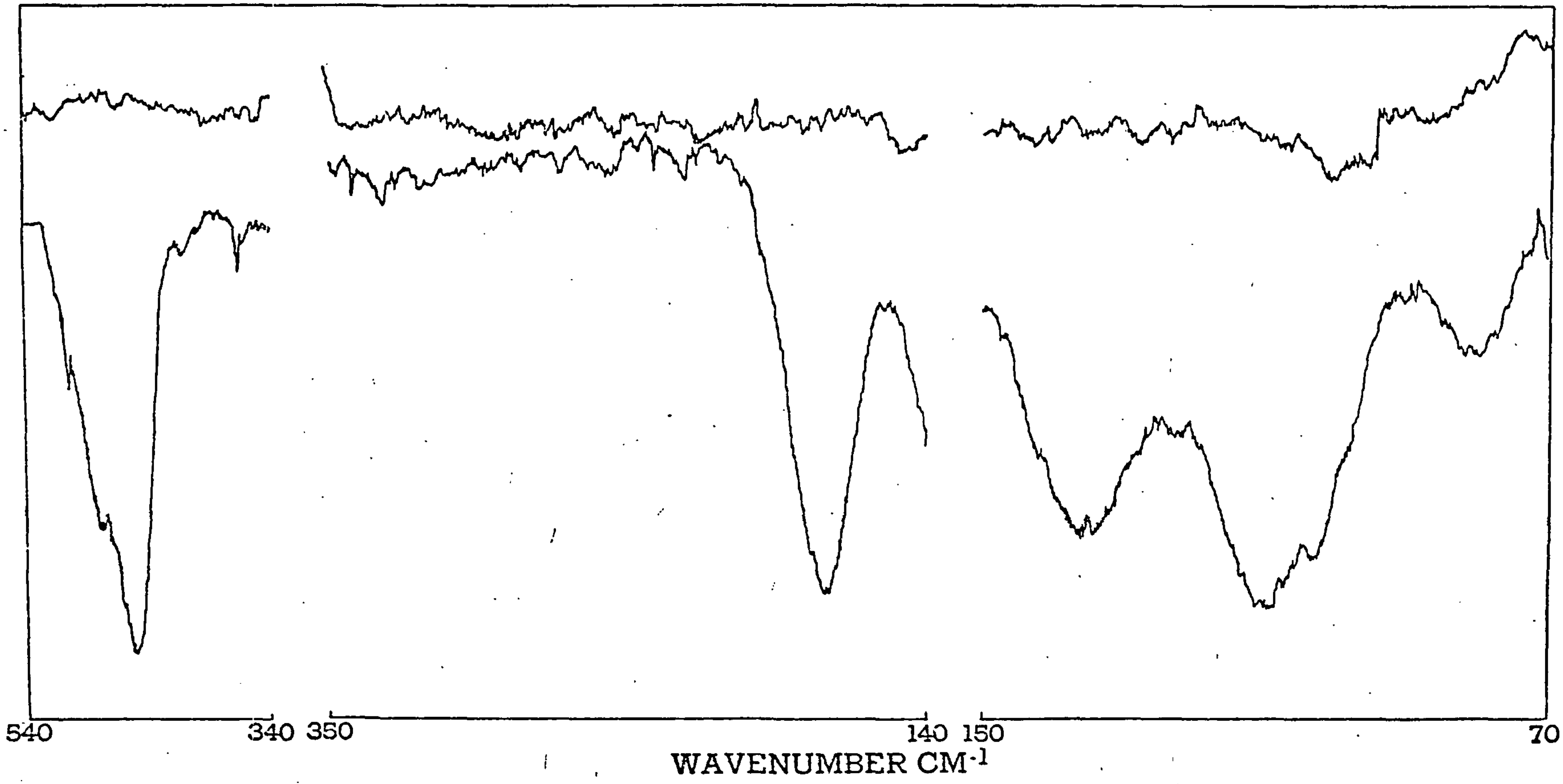
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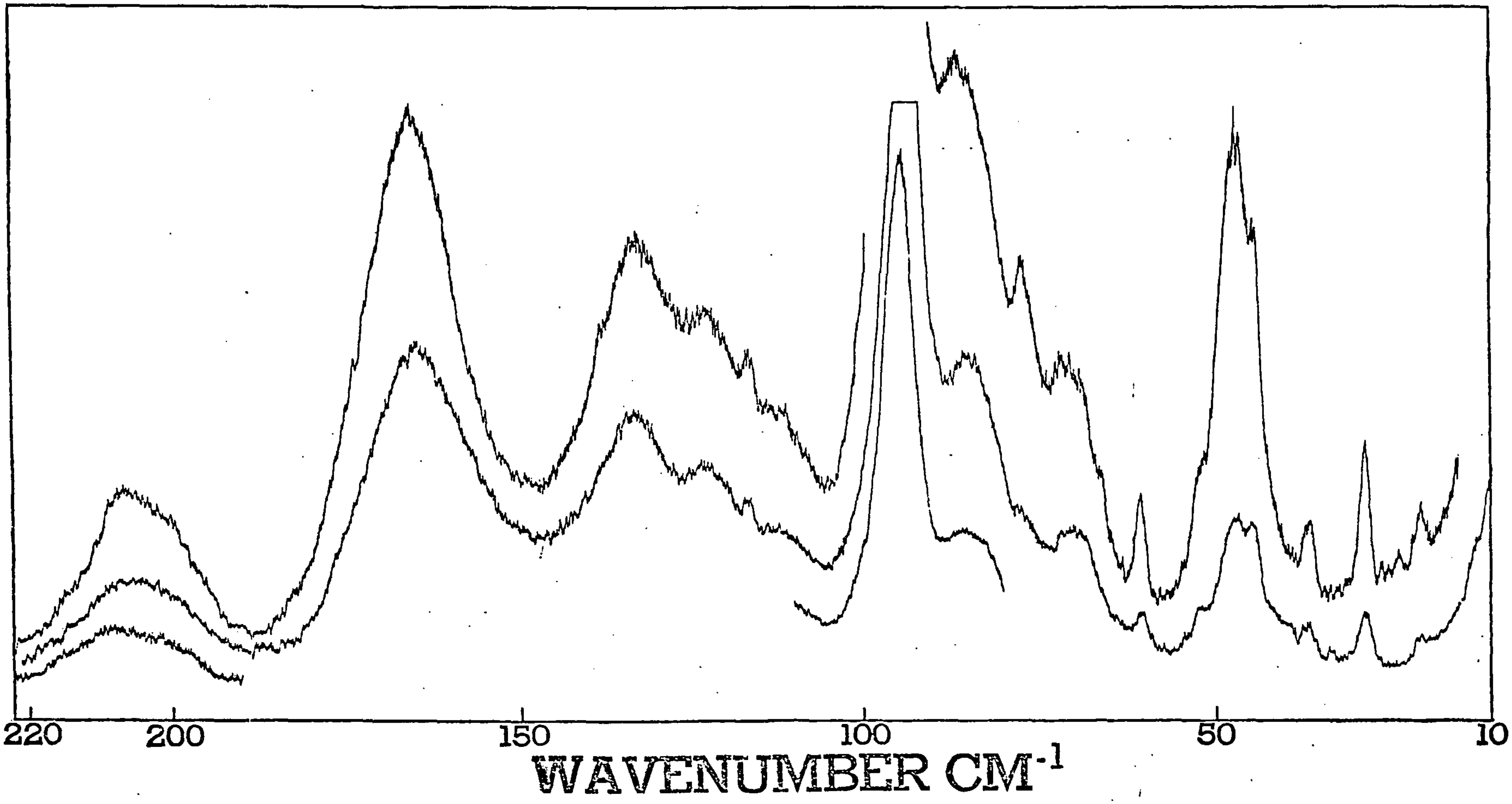
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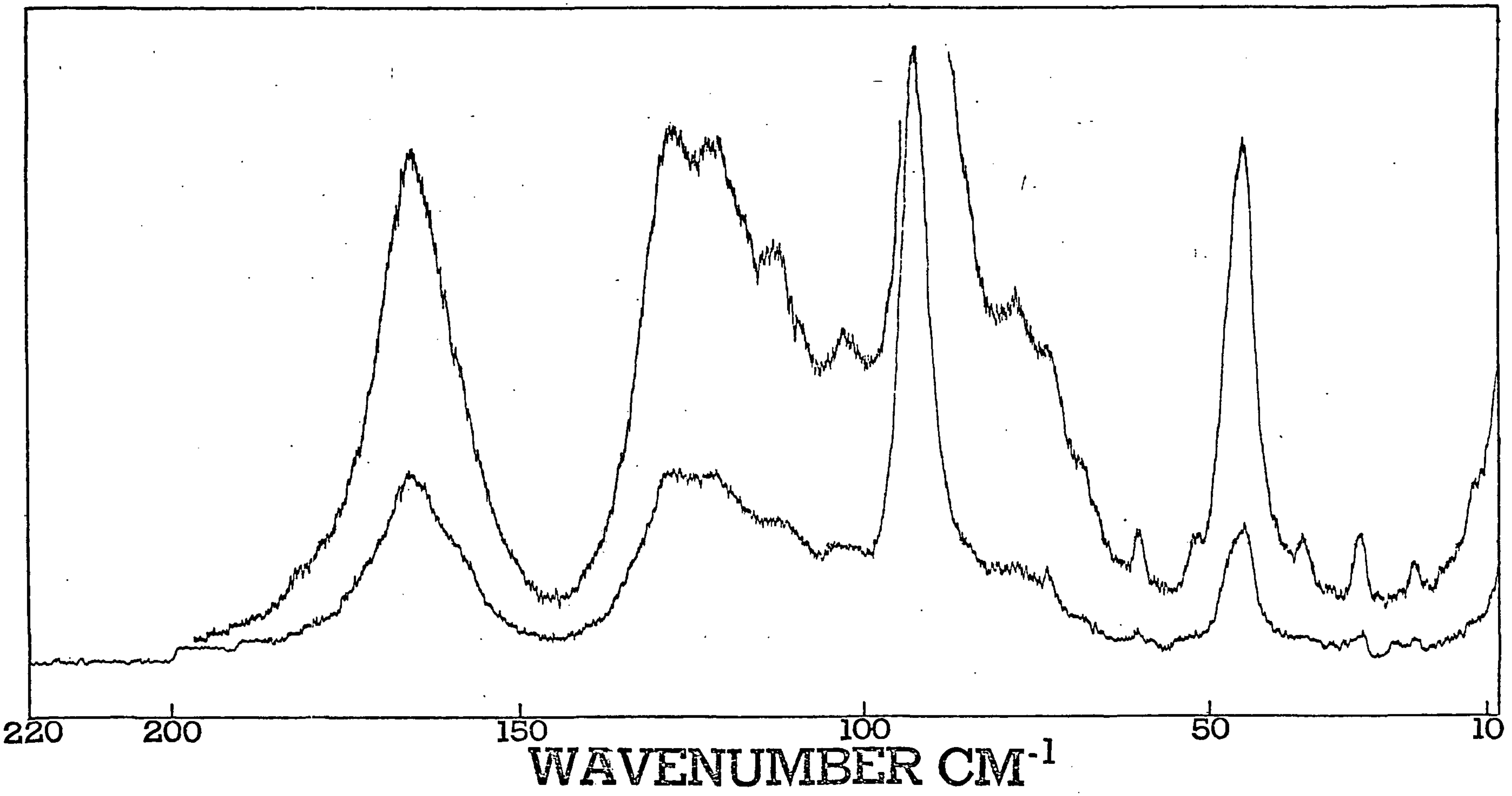
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