Journal of Molecular Structure, 129 (1985) 45-56 Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

# FAR INFRARED SPECTRA AND BARRIERS TO INTERNAL ROTATION OF BENZALDEHYDE, BENZOYL FLUORIDE, BENZOYL CHLORIDE AND ACETOPHENONE

J. R. DURIG, H. D. BIST\*, K. FURIC\*\*, J. QIU\*\*\* and T. S. LITTLE Department of Chemistry, University of South Carolina, Columbia, SC 29208 (U.S.A.) (Received 14 January 1985)

### ABSTRACT

The far infrared  $(250-40 \text{ cm}^{-1})$  spectra of gaseous benzaldchyde, benzoyl fluoride, benzoyl chlonde and acetophenone have been recorded The fundamental CHO torsion for benzaldehyde has been observed at 110.85 cm<sup>-1</sup> with three excited states at 109.51, 106 52 and 104.17 cm<sup>-1</sup> along with several "hot bands" arising from the low frequency bending modes The corresponding fundamental for benzoyl fluoride has been observed at 63.36 cm<sup>-1</sup> with one well defined excited state at 61.91 cm<sup>-1</sup>. Similarly, bands observed at 44.6 and 49.5 cm<sup>-1</sup> in the spectra of benzoyl chloride and acetophenone, respectively, have been assigned to the fundamental CXO torsions of these molecules These data have allowed for the determination of the twofold berrier which governs the internal rotation of the CXO molety and have been found to be 1611 cm<sup>-1</sup> (4.61 kcal mol<sup>-1</sup>). 1739 cm<sup>-1</sup> (4.97 kcal mol<sup>-1</sup>), 1162 cm<sup>-1</sup> (3.32 kcal mol<sup>-1</sup>) and 1103 cm<sup>-1</sup> (3.15 kcal mol<sup>-1</sup>) for the aldehyde, fluoride, chloride and ketone, respectively. These results are compared to previously obtained values for two of the molecules and to some corresponding barriers for several related molecules

### INTRODUCTION

We have recently undertaken investigations of the rotational and vibrational spectra of molecules containing the CXO molety (where X = H, F, Cl, Br and CH<sub>3</sub>) [1-8]. These studies have allowed for the determination of conformational stabilities, energy differences between conformations, barners to internal rotation and in some cases structural parameters. We have concluded that the cyclopropyl carbonyl halides [4, 5] and ketone [7] exist as a mixture of *cis* and *trans* conformers (i.e., carbonyl orientation relative to the three-membered rng) and that the preferred conformation and percentage distribution between the conformers is not only dependent on the

<sup>\*</sup>Permanent address: Department of Physics, Indian Institute of Technology, Kanpur – 206016, U.P., India.

<sup>\*\*</sup>Perm: nent address: Rudjer Boskovic Institute, 41001 Zagreb, P.O. Boz 1016, Croa-ia, Yugoslavia.

<sup>\*\*\*</sup>Taken in pert from the thesis of J. Qiu which will be submitted to the Department of Chemistry in partial fulfillment of the M.S. degree.

halide or methyl group but also on the phase which is investigated. These results are in direct contrast to what was found for propionyl fluoride [6] where we have concluded that this molecule exists in a *cis* (i.e., carbonyl orientation relative to the methyl group) and gauche conformational equilibrium. The microwave and far-infrared results obtained for isopropylcarboxaldehyde [8] indicate that this molecule also exists as a cis (i.e., carbonyl orientation relative to the a-hydrogen) and gauche equilibrium. Similar studies have been carried out for the propenoyl halides [1] and methyl vinyl ketone [2] and it has been shown that these molecules exist as cis and trans coulibria. Although, in many cases, a large amount of data could be found in the earlier literature for these molecules, our studies [1-8] have clarified ambiguities in the relative stabilities of existing conformers and have provided barners to internal rotation and the potential constants governing this molecular motion. As a continuation of these studies we have investigated the far-infrared spectra of a series of benzoyl compounds to obtain the twofold barriers to internal rotation.

Kakar and co-workers [9, 10], as a result of their microwave investigations of benzaldehyde [10] and benzoyl fluoride [9], have determined that these molecules have planar structures Furthermore, the larger value of the inertial defect determined for the fluoride ( $-0.325 \text{ U A}^2$ ) compared to the corresponding quantity for the aldehyde ( $-0.128 \text{ U A}^2$ ) has been attributed to the fluonde simply having a heavier internal rotor compared to the aidehyde and not to the CFO molety lying slightly out-of-plane. From relative intensity measurements, these authors were able to determine the fundamental frequencies of the CXO torsional modes to be 113.8 = 5.0 and  $59.5 \pm$  $3 \text{ cm}^{-1}$  for the aldehyde [10] and fluoride [9], respectively. Subsequent barrier height calculations yielded values of  $1714 \text{ cm}^{-1}$  (4.90 ± 0.43 kcal  $mol^{-1}$ ) and 1560 ( $m^{-1}$  (4.46 ± 0.46 kcal  $mol^{-1}$ ) for the aldehyde [10] and fluonde [9], respectively. These authors [9, 10] state further that the difference between the determined barrier heights for the two molecules should probably be greater if conjugation between the ring and rotating group were solely responsible for the barner heights.

The fundamental CHO torsion of benzaldehyde has been observed at  $111 \text{ cm}^{-1}$  in the far infared spectrum of the vapor [11]; however, successive excited states were not identified. This assignment of the CHO torsional fundamental was later venified but again no "hot bands" were reported [12]. Therefore, there has not been any previous attempt to evaluate the  $V_4$  term in the potential function for this molecule although the barrier appears to have been reasonably well determined [11].

To our knowledge, similar microwave studies of benzoyl chloride and acetophenone have not been carried out; however, an extensive amount of vibrational data currently exists in the literature for both of these molecules [13-18]. The most recent of these studies appears to be for acetophenone where Gambi et al. [13] have carried out an extensive infrared study of the parent molecule and the  $-d_3$ ,  $-d_5$  and  $-d_8$  analogs. From this investigation, they determined a valence force field which was used to support their assignment of a planar structure where two of the methyl hydrogens lie above and below the plane while the third lies in the plane itself. Although they clearly state that the methyl and CXO torsions were not observed, and thus remain unidentified, frequencies of 74 and 23 cm<sup>-1</sup>, respectively —ore calculated for these modes in the parent compound. There appears to be one case where the C(CH<sub>3</sub>)O torsion was observed for acetophenone [11] and the frequency reported was  $48 \pm 2$  cm<sup>-1</sup>. Although these authors [11] calculated a barrier height of 1084 cm<sup>-1</sup> (3.1 kcal mol<sup>-1</sup>), they state that the observed contour is very broad and a considerable amount of uncertainty exists in the observed frequency and, consequently, in the barrier height.

Similar infrared studies have been carried out for benzoyl chloride [14– 17]; however, the CClO torsional fundamental has not been observed. From one of these studies [15], it is stated that an extensive investigation of the infrared spectrum to 75 cm<sup>-1</sup> gave no indication of this mode and thus these authors concluded that it must lie below this frequency.

The development of far-infrared interferometry as a means of investigating low-frequency torsional vibrations has produced a number of interesting results [18]. These results have clarified the relative conformational energies of a number of molecules and have allowed for more accurate determinations of the potential functions which govern the internal rotations. We have, therefore, carried out an investigation of the far-infrared spectrum of the vapor phase of benzaldehyde with the hope of more accurately determining the barner height and to ascertain whether the potential contains a  $V_4$  term. Similar studies have been carried out for benzoyl fluoride, benzoyl chloride and acetophenone for comparative purposes. The results of these studies are reported herein.

### EXPERIMENTAL

Benzoyl fluoride was prepared by the reaction of benzoyl chloride (Aldrich Chemical Co.) with an excess of  $SbF_3$  The mixture was stirred vigorously for 1 hour at about 60°C, and the product was subsequently removed from the reaction mixture by distillation. The sample was purified by using a lowtemperature sublimation column. Both benzalcheyde and acetophenone were obtained from Fisher Scientific Company with stated puncties of 99+% and were used without further punctication. Traces of water were removed by passing the gaseous samples through dried 3 Å molecular sieves.

The far-infrared spectra of the gases were obtained with a Nicolet model 8000 Fourier transform interferometer equipped with a vacuum bench and a helium cooled Ge bolometer containing a wedged sapphire filter and polyethylene windows. Both 6.25 and 12 5  $\mu$  Mylar beamsplitters were employed depending on the frequency region under investigation, and the samples were contained in either a 1 m or a 20 m cell. The effective resolution was 0.12 cm<sup>-1</sup> and 256 interferograms were taken for both the sample and reference cell. These interferograms were averaged and transformed by using a boxcar apodization function. The spectral data are shown in Figs. 1-4 and the frequencies listed in Tables 1 and 2 are expected to be accurate to at least  $\pm 0.05$  cm<sup>-1</sup> for the sharp Q branches.

# RESULTS

### Benzaldehyde

The far-infrared spectrum of gaseous benzeldehyde is characterized by two absorptions below 250 cm<sup>-1</sup> (Fig. 1). The first of these occurs at 223.8 cm<sup>-1</sup> and is assigned to the ring-CHO out-of-plane bend based on its C-type contour. A series of "hot bands" which probably proceed to higher frequency is associated with this bending fundamental and they have been attributed as arising from the CHO torsion. However, it is possible that the fundamental is the highest frequency band with successive excited states falling to lower frequency. Therefore, there is ambiguity as to whether the fundamental is at 225.2 or 223.8 cm<sup>-1</sup> and we have rather arbitrarily chosen the lower frequency. The most interesting feature of this band is that the four Q-branches

### TABLE 1

ν (cm <sup>-1</sup> )	Relative intensity	Assignme it	Obs. — calc. <sup>b</sup>
225 2 Q	<u>m</u>	hot band	
224.7 Q	m	hot band	
224 4 Q	m	het band	
220.8 Q	m	out-of-plane bend	
~214 min	m	in-plane bend	
110.85 Q	m	$1 \leftarrow 0$ torsion	-0 30
110.55 Q	mw	hot band	
110.28 Q	mw	hot band	
110 05 Q	w	hot band	
109 51 Q	<b>D</b> )	2 1 torsion	0.65
109.25 Q	w	hot band	
107.65 Q	TV	hot bard	
106.52 Q	17	$3 \leftarrow 2$ torsion	-0.03
106.23 Q	w	hot band	
105.85 Q	VW	hot band	
105.64 Q	R	hot band	
105.13 Q	VW	hot band	
$10417\hat{Q}$	w	4 ← 3 torsion	-0.05

Observed<sup>3</sup> bands and proposed assignments of the infrared spectrum of gaseous benzaldehyde below 250 cm<sup>-1</sup>

<sup>a</sup>Abbreviations used m, medium, w, weak, v, very; min, minimum. <sup>b</sup>Calculated using potential constants and F-number given in Table 3.

#### TABLE 2

Molecule	$\nu (\mathbf{cm}^{-1})$	Relative intensity	Assignment
Benzoyì fluoride	225 R?	w, bd	$158 \neq 62 = 221 ?$
	212.7 Q	m	in-plane bend
	~204	m, sh	?
	158.0	w	out-of-plane bend
	63.36	vw	$1 \leftarrow 0$ torsion
	61.91	vw	$2 \leftarrow 1$ torsion
Benzoyl chloride	200.5	m	n-plane bend
	~170	w	out-of-plane bend
	44.6	m	1 ← 0 torsion
Acetophenone	219 3	m	ın-plane bend
	188 5	w	cut-of-plane bend
	49 5	m	1 ← 0 torsion

Observed<sup>a</sup> bands and proposed assignment of the far-infrared spectrum below 250 cm<sup>-1</sup> of gaseous benzoyl fluoride, benzoyl chloride, and acetophenone

<sup>a</sup>Abbreviations used. bd, broad; m, medium; sh, shoulder, v, very; w, weak.

all have nearly the same intensity and that they er d rather abruptly after the third "hot band". This band also has a pronounced low-frequency st oulder which appears to have a minimum at 214 cm<sup>-1</sup> and this band has been assigned to the in-plane bend. The assignment of these two fundamentals is reversed from that given previously [12] but the sharp Q-branches on the 224 cm<sup>-1</sup> band center require that this band be assigned to the out-of-plane motion.

The second far-infrared absorption band is found at 110.85 cm<sup>-1</sup> and it is about one-half as intense as the out-of-plane bending mode. It is also a type C band but the successive excited states (Fig. 2) clearly fall to lower frequency and this band can be confidently assigned as the CHO torsion. In addition to the fundamental at 110.85 cm<sup>-1</sup> this Q-branch has three "hot



Fig. 1 Far-infrared spectrum of benzaldehyde from 250 to 80 cm<sup>-1</sup>.



Fig. 2. Torsional transitions of benzaldehyde. The top spectral trace is t iat of water.

bands" occurring at 110.55, 110.28 and 110.05  $\text{cm}^{-1}$  with which it is apparently associated These bands cannot be attributed to excited states of the CHO torsion because of the relative close spacing of the successive transitions. Furthermore, if such an assignment is made, then the remaining Qbranches, which fall to lower frequency in the spectrum, would be left unassigned. Therefore, we have assigned this first series of "hot bands" as arising from the CHO torsion in successive excited states of a bending fundamental. The next strongest Q-branch below  $110.85 \text{ cm}^{-1}$  occurs at  $109.51 \text{ cm}^{-1}$ and it is reasonable to assign this Q-branch to the  $2 \leftarrow 1$  transition of the CHO torsion. Similarly, the 6'-branches observed at 106.52 and 104.17 cm<sup>-1</sup> can be assigned to the  $3 \leftarrow 2$  and  $4 \leftarrow 3$  torsional transitions, respectively. It is interesting to note that a series of Q-branches is associated with the  $2 \leftarrow 1$ and  $3 \leftarrow 2$  transitions as was the case for the  $1 \leftarrow 0$  transition. However, for the excited torsional states they are not as clearly defined and the  $2 \leftarrow 1$  transition appears to be perturbed since it is closer to the fundamental than one would predict from the spacing of the higher transitions (Fig. 2). We [19] have recently observed similar "hot bands" in the far infrared spectrum of 3-fluoropropene and have attributed the additional "fine" structure which is observed on the fundamental asymmetric torsion and the successive excited states as ansing from the CH<sub>2</sub>F asymmetric torsion in excited states of the FCC and CCC bending modes The assignment of the observed far infrared data below 250 cm<sup>-1</sup> is summarized in Table 1.

# Benzoyl fluoride

Unlike the far-infrared spectrum of benzaldehyde, which is characterized by only two well-defined absorptions below  $250 \text{ cm}^{-1}$ , the far-infrared spectrum of the corresponding fluoride is relatively complex with three or possibly four absorptions below this frequency. The first of these appears as a broad absorption centered at 213  $\text{cm}^{-1}$  (Fig. 3). It is not clear whether the shoulder at 225  $cm^{-1}$  is a band centered at this frequency or whether it is the *R*-branch of a *B*-type band centered at about 222 cm<sup>-1</sup>. Irrespectively, we have tentatively assigned this band as a combination of the out-of-plane bend at 158 cm<sup>-1</sup> with the CFO torsion. The in-plane bend is confidently assigned to the band centered at 213 cm<sup>-1</sup> but there appears to be a low-frequency shoulder centered at 204 cm<sup>-1</sup> which may have two Q-branches associated with it. This absorption is either the CTO wagging motion, which has previously been assigned [20] at 699  $cm^{-1}$ , or a difference band which is presumably more probable. The remaining band to be assigned in the far-infrared spectrum of benzoyl fluoride is the CFO symmetric torsion and we have observed two well-defined Q-branches at 63.36 and 61.91  $\text{cm}^{-1}$  which are assigned as the  $1 \leftarrow 0$  and  $2 \leftarrow 1$  transitions, respectively (Fig. 3). As for the bending fundamentals, additional well-defined features have not been observed, as was the case for the aldehyde. It is probable that there are many excited states associated with the bending modes and they simply are not being resolved with the resolution of  $0.12 \text{ cm}^{-1}$ . In fact, there are indications of shoulders on the  $1 \leftarrow 0$  transition and there are clear absorptions at two additional places lower in frequency than the  $2 \leftarrow 1$  transition, but there are no well-defined Q-branches in these regions which could be assigned to the



Fig. 3. Far-infrared spectrum of denzoyl fluoride from 235-135 cm<sup>-1</sup> and from 70-54 cm<sup>-1</sup> (upper trace is water, center trace shows intensity of the torsional transitions relative to the bending fundamental, and the lower trace is an expansion of the torsional transitions).

higher transitions The assignment of the far-infrared spectrum of benzoyl fluoride is summarized in Table 2.

### Benzoyl chloride

The far-infrared spectrum of benzoyl chloride, below 250 cm<sup>-1</sup>, appears to be characterized by three absorption bands centered at 200.5, ~170 and 44.5 cm<sup>-1</sup> but none of these bands appear to have any distinct contours. The band at 200.5 cm<sup>-1</sup> has been assigned as the in-plane bending mode and the cne at ~170 cm<sup>-1</sup> has been assigned to the mass sensitive out-of-plane ring mode. This latter assignment must be considered tentative since the corresponding Raman line in the liquid phase has been reported [15] at 167 cm<sup>-1</sup>. Also the relative intensity is considerably stronger than the correspondingly assigned mode in the benzoyl fluoride molecule. Therefore, there is a distinct possibility that the infrared band does not correspond to the observed Raman line [15] which would then require the assignment of another fundamental in this region or the presence of a difference band.

The remaining band in the far-infrared spectrum is centered at approximately 44.6 cm<sup>-1</sup> and it is undoubtedly the CCIO torsion. Although there may be two additional Q-branches the quality of the spectrum was not sufficient to confidently assign any excited states. It is probable that there are many "hot bands" associated with each excited state which would require considerably higher resolution to resolve them distinctly. The assignment of the far infrared spectrum of benzoyl chloride is summarized in Table 2.

### Acetophenone

The far infrared spectrum of gaseous acetophenone is very similar to that of benzovl chloride except the bands are centered at 219.3, 188.5 and 49.5 cm<sup>-1</sup>. The former of these three is presently assigned to the in-plane bending mode and the 188.5 cm<sup>-1</sup> band is assigned to the mass sensitive outof-plane ring mode. As with the chloride, this latter assignment must be considered tentative since the corresponding Raman line has been reported [20] in the liquid phase at  $165 \text{ cm}^{-1}$ . A similar alternative assignment can thus be proposed for acetophenone where it is possible that the 188.5  $cm^{-1}$  band is the CCH<sub>3</sub>O wag (previously assigned [20] at 695 cm<sup>-1</sup>) which would necessitate that the Raman line at 165 cm<sup>-1</sup> be assigned to the out-of-plane ring mode. The final band, centered at 49 5 cm<sup>-1</sup>, is assigned to the  $C(CH_3)O$  torsion. The CH<sub>3</sub> torsion has not been presently assigned; however, this vibration is typically very weak for ketones. This vibration has been calculated [13] to occur at 74  $cm^{-1}$ ; however, based on results which we have obtained for several other ketones, we suspect that it is in the range of  $110 \text{ to } 130 \text{ cm}^{-1}$ . The assignment of the observed far-infrared bands of acetophenone is listed in Table 2.



Fig 4. Far-infrared survey spectrum of acetophenone from 250 to 30 cm<sup>-1</sup>.

### BARRIERS

Using the assignments given in Tables 1 and 2 for the torsional transitions, the twofold symmetric torsional potential functions of benzaldehyde, benzoyl fluoride, benzoyl chloride, and acetophenone have been calculated. The periodic barriers to internal rotation of the CXO moieties have been determined with the use of a computer program similar to the one described by Lewis et al [21], in which the torsional potential can be represented as a Fourier cosine series in the internal rotation angle

$$2V(\theta) = V_2(1 - \cos 2\theta) + V_4(1 - \cos 4\theta)$$

where  $\theta$  is the torsional angle. The program determines the coefficients  $V_2$ and  $V_4$  from the input of the observed torsional transitions and the structurally dependent internal rotation constant F which is equal to  $h^2/8\pi^2 cI_r$ , where  $I_r$  is the reduced moment of inertia for the top. The potential constants for the ngid rotation of the CXO moieties listed in Table 3 were obtained by utilizing the F numbers previously suggested from the microwave investigations [9, 10] or calculated from reasonably assumed structural parameters. For benzaldehyde, both the  $V_2$  and  $V_4$  terms were calculated. The  $V_2$  term represents the barrier height and arises from the twofold nature of the CHO rotational potential whereas the relatively small  $V_4$  term serves to "shape" the twofold well. For the other molecules only the  $V_2$  term was calculated

### TABLE 3

Potential constants (cm<sup>-1</sup>) for the symmepical twofold barriers of benzaldehyde, benzoyl fluoride, benzoyl chloride and acetophenone

Molecule		Dispersion	$V_4$	Dispersion
benzaldehyde $(F = 1.890 \text{ cm}^{-1})$	1611	22	22	7
benzoyl fluoride ( $F = 0.5790 \text{ cm}^{-1}$ )	1739	14		
benzoyl chloride ( $F = 0.4369 \text{ cm}^{-1}$ )	1162	40		
acetophenone ( $F = 0.5681 \text{ cm}^{-1}$ )	1103	35		

because of the lack of confidently assigned excited torsional transitions. The calculated twofold barriers are 1611 cm<sup>-1</sup> (4.61 kcal mo<sup>-1</sup>), 1739 cm<sup>-1</sup> (4.97 kcal mol<sup>-1</sup>), 1162 cm<sup>-1</sup> (3.32 kcal mol<sup>-1</sup>), and 1103 cm<sup>-1</sup> (3.15 kcal mol<sup>-1</sup>) for the aldehyde, fluonde, chloride and ketone, respectively. These results are summarized in Table 3. The dispersions listed for the aldehyde and fluonde are twice the statistical standard deviations whereas those for the chloride and ketone are estimated on the basis of the choice of the band center of the torsional fundamental.

## DISCUSSION

In the far infrared spectrum of benzoyl fluoride, benzoyl chloride and acetophenone there appears to be a band which is somewhat higher in frequency than the Raman line for the liquid phase which has previously been assigned to the mass sensitive ring-CXO out-of-plane bending mode. Since fundamental vibrations below 200 cm<sup>-1</sup> shift to higher frequency in going from the gas to the liquid this infrared band probably does not correspond to this normal mode. Thus, it appears that there is a good probability that one of the CXO bending modes may be misassigned for all of these molecules or that a very unusual shift occurs in going from the gaseous to the liquid state Further infrared and Raman studies of all of these molecules in the solid state would probably help to clear up this point.

The determined barriers provide an interesting grouping. The barriers for the aldehyde and fluoride are relatively high with values of 4 61 and 4.97 kcal mol<sup>-1</sup>, respectively, and both molecules have been shown to be planar by microwave studies [9, 10]. The chloride and ketone have barrier values of 3.32 and 3.15 kcal mol<sup>-1</sup>, respectively, which are significantly lower than the aldehyde and fluoride, but the results cannot be attributed to the electronegativity effects of the X group. However, it should be noted that the chlorine atom and the methyl group have similar van der Waals' radii so steric effects could be playing the dominant role. In fact, it is possible that these latter two molecules are not planar, which would reduce the conjugation and lower the barrier. It would be interesting to carry out microwave studies on these two compounds to determine whether the CXO group is out of the plane of the ring.

The slightly lower barrier of 4.61 kcal mol<sup>-1</sup> for benzaldehyde compared to the value of 4.90 kcal mol<sup>-1</sup> (5.28 kcal mol<sup>-1</sup> for  $C_sH_sCDO$ ) from the microwave study [10] is the result of the observed frequency being lower than the higher estimated frequency of 113 cm<sup>-1</sup> for the torsional fundamental Similarly, our barner of 4.97 kcal mol<sup>-1</sup> for the fluoride compared to the value of 4.46 kcal mol<sup>-1</sup> obtained from the estimated frequency of 59.5 cm<sup>-1</sup> for the torsional fundamental from the relative intensities of microwave transitions [9] is the result of the higher frequency observed for this fundamental. As pointed out by Kakar [9] an uncertainty of 3 cm<sup>-1</sup> in the torsional frequency results in an uncertainty of 0.45 kcal mol<sup>-1</sup> in the barrier value for the fluoride. Since it is very difficult to obtain frequencies to better than  $\pm 5$  cm<sup>-1</sup> for vibrations in the 60 cm<sup>-1</sup> region from microwave relative intensities, the barriers obtained by such measurements have a relatively large uncertainty associated with them.

The small value of 0.06 kcal mol<sup>-1</sup> for the  $V_4$  term for the potential governing the internal rotation for benzaldehyde is consistent with the small values obtained for the  $V_6$  terms for threefold barriers [22]. Therefore, it appears that confident barrier values for twofold rotors can be obtained from only the  $1 \leftarrow 0$  transitions since it is expected that the  $V_4$  terms of other twofold rotors will also be small.

Silver and Wood [23] obtained the internal rotational barriers of benzaldehyde and the orthc-. meta-, and para-substituted chlorides from a study of the far-infrared spectra of the liquids. It should be noted that large differences in the barrier values are obtained between the liquid (6.68 kcal mol<sup>-1</sup>) and gas (4.61 kcal mol<sup>-1</sup>) in benzaldehyde because of the large shift in the torsional frequency with condensation due to the intermolecular forces in the liquid. Therefore, companison of barrier values for compounds in the liquid state may not reflect those obtained for the gaseous state since the intermolecular forces in the different liquids are expected to be significantly different, which will result in different shifts of the torsional frequencies. Therefore, it would be interesting to compare the values of the barriers for several series of substituted benzaldehydes in the gas phase to determine the effect on the barriers in those compounds with substituents having different inductive effects.

One of the more interesting aspects of this study is the apparent perturbation of the  $2 \leftarrow 1$  torsional transition in benzaldehyde. This band is  $0.65 \text{ cm}^{-1}$ closer to the fundamental transition than predicted from the potential function and there is a second pronounced line at 107.65 cm<sup>-1</sup> which is displaced to a lower frequency by about the same amount from the calculated transition. In fact, it was not entirely clear which of these transitions corresponds to the  $2 \leftarrow 1$  transition. A similar perturbation was found in the far-infrared spectrum of propanal [24]. Also, it should be noted that only three excited states of the CHO torsion in benzaldehyde were observed which is exactly the number observed for the *gaucke* conformer of isopropylcarboxaldehyde [8]. Therefore, the torsional manificians for the CHO moiety seem to differ from those of other CXO groups. It is possible that further studies of the CXO torsional modes for enveral other molecules might provide additional insight into why these distinct ons are present for the aldehyde moiety.

### ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of this study by the National Science Foundation through the Yugoslavian—American Scientific Exchange Program by Grant YOR 81-029 and by Grant CHE-83-11279.

#### REFERENCES

- 1 J. R. Durig, J. S. Church and D. A. C. Compton, J. Chem. Phys., 71 (1979) 1175.
- 2 J. R. Durig and T S. Little, J. Chem. Phys., 75 (1981) 3660
- 3 J. R. Durig, P. A. Brletic and J. S. Church, J. Chem. Phys., 76 (1982) 1723.
- 4 J R. Durig, H. D. Bist and T. S. Little, J. Chem. Phys., 77 (1982) 4884.
- 5 J. R. Durig, H. D. Bist, S. V. Saari, J. A. Smooter Smith and T. S. Little, J. Mol. Struct, 99 (1983) 217.
- 6 G. A. Gurgis, B. A. Barton, Jr. and J. R. Durig, J. Chem. Phys., 79 (1983) 5918
- 7 J R. Dung, H. D. Bist and T. S. Little, J. Mol. Struct., 116 (1984) 345.
- 8 J. R. Durig, G. A. Gurgis, T. S. Little and O. L. Stiefvater, Thirty-ninth Symposium on Molecular Spectroscopy, The Ohio State University, 1984, paper MH10.
  9 E. K. Kahara, J. Cham. Bhys. 56 (1972) 1180.
- 9 R. K Kakar, J. Chem. Phys., 56 (1972) 1189.
- 10 R K. Kakar, E. A. Rinehart, C. R. Quade and T. Kojima, J. Chem. Phys, 52 (1970) 3803.
- 11 F A Miller, W G. Fateley and R. E. Witkowski, Spectrochim. Acta, Part A, 23 (1967) 891.
- 12 J. H. S Green and D. J. Harrison, Spectrochim. Acta, Part A, 32 (1976) 1265.
- 13 A Gambi, S. Giorgianni, A. Passerini, R. Visinoni and S. Ghersetti, Spectrochim. Acta, Part A, 36 (1980) 871.
- 14 C. Garrigou-Lagrange, N. Claverie, J. M. Lebas and M. L. Josien, J. Chim. Phys, 58 (1961) 559.
- 1. D. A. Condit, S. M. Craven and J. E. Katon, Appl. Spectrosc., 28 (1974) 420.
- 16 S. C. Sırkar and P. K. Bishui, Ind. J. Phys., 42 (1968) 243.
- 17 P. Delorme, V. Lorenzelli and A. Alemagna, J. Chim. Phys., 62 (1965) 3.
- 18 D. A. C Compton, in J R Durig (Ed.), Vibrational Spectra and Structure, Elsevier, Amsterdim, 1981, Vol. 9, p. 255.
- 19 J R. Durig, Mengzhang Zhen and T S Little, J. Chem. Phys., 81 (1984) 4259.
- 20 J. H. S. Green and D. J. Harrison, Spectrochim. Acta, Part A, 23 (197?) 583.
- 21 J. D. Lewis, T. B. Malloy, Jr., T. H. Chao and J. Leane, J. Mol. Struct., 12 (1972) 427.
- 22 J. R. Durig, S. M. Craven and W. C. Harris, in J. R. Durig (Ed.), Vibrational Spectra and Structure, Marcel Dekker, New York, 1972, Vol. 1, p. 73.
- 23 H G. Silver and J. L Wood, Trans Faraday Soc., 60 (1964) 5.
- 24 J R Durig, D A. C. Compton and A Q. McArver, J. Chem. Phys, 73 (1980) 719.