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Phosphorescence Spectra of Two Rotational Isomers of *m*-Fluorobenzaldehyde

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Phosphorescence spectra of *m*-fluorobenzaldehyde and its aldehyde deuterated derivative have been observed in the vapor phase at room temperature and in a methylcyclohexane matrix at 4.2 K. Paired band systems were detected for the vapor phase and for each of the two different crystallographic phases, α- and β-phases, and were attributed to two rotational isomers of the aldehyde group. Variable intensity changes between the two paired bands observed in the α-phase crystal are manifestations of the isomeric conversion in the ground state during crystallizations. An energy correlation of the rotational isomers between the lowest excited $n\pi^*$ singlet and triplet states is given for the vapor phase and for the α-phase methylcyclohexane matrix.

About one and a half score of years ago, several pieces of physicochemical evidence concerning rotational isomers in mono-substituted benzaldehydes were presented by molecular spectroscopists who had been engaged in ultrasonic,[1)] IR,[2—5)] and ^{1}H NMR[6,7)] spectroscopies. Dipole moment measurements,[8—10)] and ^{13}C and ^{19}F NMR studies[11,12)] followed these spectroscopies together with a few theoretical studies.[13,14)] All these studies concern information about the geometry and/or the stability energy of such molecules in the ground state. Recent technical development in supersonic jet experiments allows more clear-cut detection of two rotational isomers in such aromatic aldehydes. Among them there is an archetypical aldehyde, *m*-fluorobenzaldehyde (hereafter abbreviated as mFB). Recently Yamamoto, Ebata, and Ito (Y–E–I) studied $^{1,3}n\pi^* \leftarrow S_0$ phosphorescence excitation spectra and succeeded in detecting two rotational isomers in the spectra.[15)]

Prior to this, Haque and Thakur (H–T) observed a well-resolved phosphorescence spectrum in the vapor phase at room temperature and found two intense bands having a separation of 32.7 cm^{-1} in the origin band region and in other prominent vibronic band regions.[16)] They assigned the shorter wavelength component to be due to the intrinsic origin band (0_0^0) while the longer one due to a sequence band (35_1^1), where ν_{35} (in Mulliken's numbering) corresponds to the CHO-wagging (a″) vibration. The wavelengths of these bands, however, are in good agreement with a pair of the origin bands reported by Y–E–I. In an earlier paper, H–T also discussed rotational isomerism in halo-benzaldehydes from the viewpoint of electronic spectroscopy for the first time.[17)] Several possible patterns of the $n\pi^*$ electronic spectra for such molecules were pointed out in terms of intramolecular hydrogen bonds.

Furthermore, the internal rotation structures of several *ortho*- and *meta*-substituted phenols and toluenes have been clarified using the supersonic jet and laser techniques.[18—22)] As for benzaldehyde and its derivatives, however, nobody has so far succeeded in analyzing the CHO-torsional potential surface. In a hindered rotation analysis of such aromatic molecules, benzaldehydes are at a disadvantage because of (1) less fluorescence quantum yield and (2) less (or almost no) progression of the CHO-torsional vibration which may be attributed to very close potentials along the CHO-rotational vibrational coordinates with a very high barrier height for both the ground and excited states. These prevent us from determining the potential surfaces.

In previous papers we presented a partial analysis of the CHO-torsional sequence bands, $[\tau_{\mathrm{CHO}}]_i^i$ ($i = 1,2,3\cdots$), in the vapor phase phosphorescence spectra of benzaldehyde[23)] and *p*-fluorobenzaldehyde[24)] at room temperature. A few pieces of evidence for an increase (for the former) and a decrease (for the latter) in the CHO-torsional sequence frequency on going from the ground to the lowest $^3n\pi^*$ state have been obtained. In the hope of completing the analysis of the CHO-torsional potentials in benzaldehyde, we have begun measuring and collecting the sequence frequencies of a series of benzaldehyde derivatives. This motivates us to observe the phosphorescence spectra of mFB in the vapor phase at room temperature and, for a comparison, in rigid methylcyclohexane matrices.

Experimental

Materials. The guest molecule, mFB (a GR grade reagent from Wako Pure Chemical Industries, Ltd.), was purified by trap-to-trap distillations under vacuum. The aldehyde deuterated derivative (mFB-α-d_1) was obtained by reducing *m*-fluorobenzoyl chloride (a GR grade reagent from Tokyo Kasei Co., Ltd.) with brand-new lithium aluminium tri-*t*-butoxydeuteride {i.e., Li[AlD(*t*-BuO)$_3$]}[25)] in diethylene glycol dimethyl ether. The product was purified by repeated distillation under vacuum. The isotopic purity was found to exceed 95%, at least, from ^{1}H NMR measurements. The solvent, MCH (methylcyclohexane; a Dotite spectroscopic grade reagent), was used as received.

Sample Crystallization. Concentrations employed for rigid matrix experiments at low temperature were prepared to be ca. 10^{-3} mol dm^{-3} for almost all cases unless mentioned otherwise. The samples in homemade Pyrex® cells with 200—300 μm thickness were degassed by freeze-pump-thaw cycles and sealed off. As has been pointed out by Goodman et al.[26] and by Olszowski,[27] there exist at least two crystalline modifications in MCH. A crystallographic phase transition occurs between 113 and 142 K, depending upon the doped guest molecule employed and its concentration. The higher temperature crystal has been named α-phase modification and the lower one β-phase modification.[26,27]

Some technical effort is required to accomplish such different phase samples. The α-phase mixed crystal can be prepared as follows: First, a vitreous solid is obtained by rapidly immersing a Pyrex® cell containing the sample solution into liquid nitrogen; next, a gradual crystal whitening is attained by lifting the cell a few centimeters above the liquid nitrogen surface; and, finally, the crystallized-sample's cell is immersed again into liquid nitrogen immediately after the crystallization is completed.

The β-phase crystal, however, is more difficult to obtain. The β-phase crystals are produced by annealing beforehand-prepared α-phase crystals several times around the phase transition temperature (ca. 130 K). Only an α-phase crystal of MCH solution can often be obtained while only a β-phase mixed crystal can seldom. Such a β-phase crystal with a high quality has been obtained for a certain guest molecule in perdeuterated MCH, i.e., MCH-d_{14}.[26]

Measurements. The vapor phase emission was measured photographically on Kodak T-Max p-3200 films and photoelectrically on an EMI 9789QR photomultiplier tube using a Nalumi 3/4 m Czerny-Turner grating spectrophotometer. The emission was excited in flowing vapor from a reservoir containing liquid mFB/benzene mixture in 1/30 volume ratio by a Tesla coil discharge between platinum electrodes. The pressure was kept around 5 Torr (1 Torr = 133.322 Pa) throughout the experiments. Other experimental details were almost the same as described previously for the vapor experiments[23] and for the solid experiments.[24]

Results and Discussion

Vapor Phosphorescence Spectra. Vapor phase phosphorescence spectrum of mFB in the 400—430 nm region is shown in Fig. 1a. With a moderate resolution such as employed in the present experiment, almost all prominent bands look sharper than those of the vapor phase phosphorescence spectrum in p-fluorobenzaldehyde,[24] though slightly broader than those in benzaldehyde.[23] The difference in the band features is attributed to the difference of the rotational band contour in the three molecules. The band peak at 24984 cm^{-1} is tentatively taken as the origin band originating at the lowest level of the excited triplet state and is designated as 0.[28] This energy is in good agreement with 0_0^0 at 24984.0 cm^{-1} by H–T and 0_0^0 at 24981 cm^{-1} by Y–E–I.

There appears another strong band at 30 cm^{-1} lower than

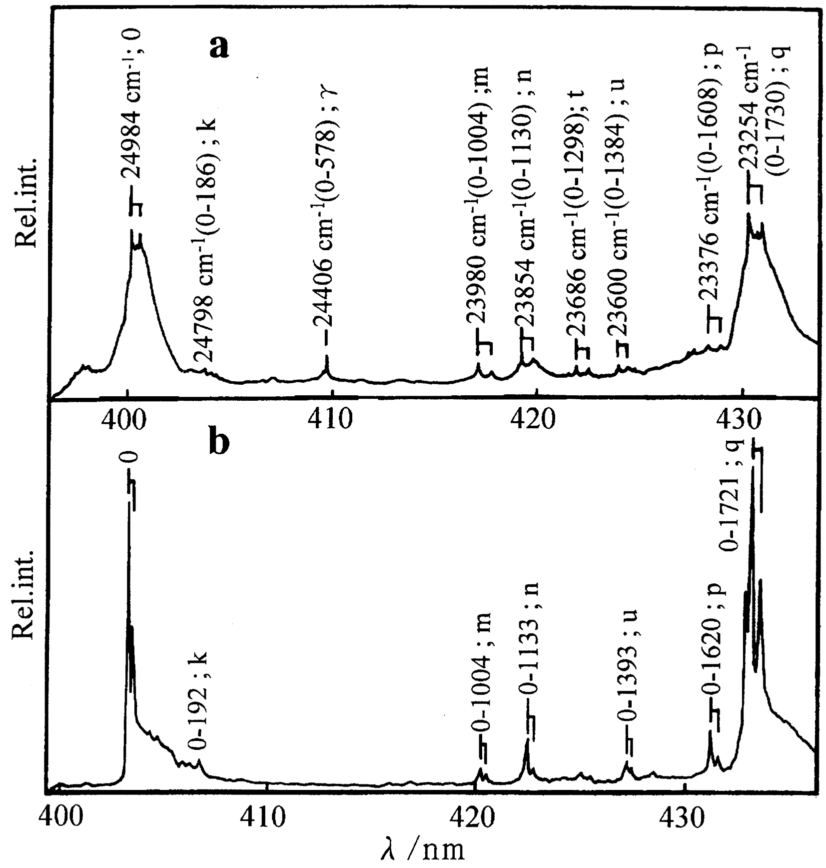

Fig. 1. Survey phosphorescence spectra of mFB (a) in the vapor phase at room temperature and (b) in an α-phase MCH matrix at 4.2 K.

this band. At a glance, the phosphorescence spectrum system looks to consist of this type of twin bands: In addition to the twin origin bands, six prominent twins with a band separation of 30—35 cm^{-1} each are observed and assigned in terms of all in-plane fundamental vibrations. All the sequence bands associated with the 0_0^0 band have also been found to be associated with the ν_6 [i.e., ν(C=O) stretching vibration] band (q) at 23254 cm^{-1}. Band q is located at 1730 cm^{-1} from the origin band. The energy separation between the paired bands in the 0–ν_6 band region is also 30 cm^{-1}, the same as that in the 0_0^0 band region. If one accepts that these twins are due to two different rotamers, the frequencies of 1730 cm^{-1} may be predicted to be almost the same for the rotamers. This prediction is the main reason why H–T did not assign the 32.7 cm^{-1} twin to the two rotamers, despite the fact that they referred to its possibility:[16,28] They suggested that in the *cis*-O rotamer of mFB the C=O stretching frequency is expected to decrease from its value in benzaldehyde (1728 cm^{-1}), at least from that in the *trans*-O because of the participation of hydrogen bonding for the former.

The most prominent bands appearing next to the 0_0^0 and 6_1^0 bands are the band n at 23854 cm^{-1} and the single peak band γ at 24406 cm^{-1}. A very close structure of the former to the 0_0^0 and 6_1^0 bands was found for the former, but not for the latter. From an analogy with vibrational analyses of benzaldehyde[23] and p-fluorobenzaldehyde,[24] the former band is assigned to one of the in-plane C–H bending vibrations, 16_1^0 ($9a_1^0$ or 9_1^0 in Wilson's numbering)[29] and the latter to 26_1^1 where the vibrational mode ν_{26} corresponds to the aldehyde out-of-plane H-wagging mode. The assignment of 26_1^1 for the -578 cm^{-1} band was taken from numerical and spectral analogies to the benzaldehyde case, for which we have studied detailed vibrational assignment of the H-wagging vibration for the ground and the ${}^3n\pi^*$ state in a series of papers.[23,26,30,31]

In the 25_0^1 band region around +170 cm^{-1}, there appear a quite few sharp bands on a photographic plate. In contrast to this, the band 25_1^0 group centered around -190 cm^{-1} appears to consist of several diffuse bands. As has previously been pointed out for benzaldehyde vapor phase spectra,[23] these hot and cold bands are expected to make a long sequence progression by combination with $[\tau_{\mathrm{CHO}}]_i^i$ ($i = 1,2,3, \cdots$). Because of the intensity weakness we have not yet succeeded in determining the structure explicitly by higher order detection, however.

Phosphorescence Spectra in MCH Matrices. Phosphorescence spectrum of mFB in an α-phase MCH matrix at 4.2 K is shown in Fig. 1b. With respect to band spacing and intensity distribution, the spectrum is considerably similar to the vapor spectrum (cf. Fig. 1a). Aside from its band position, the spectral pattern and the deuteration effect exhibit that the transition is of typical $n\pi^*$ nature (see Table 1 in which the 52 cm^{-1} blue shift of the origin band on going from mFB to mFB-α-d_1 is evaluated). Referring to the previously given analyses for benzaldehyde[23] and p-fluorobenzaldehyde,[24] assignment of main bands for mFB and its aldehyde deuterated derivative (mFB-α-d_1) is rather simple and straightforward. A tentative assignment is in part given in Table 1.

The big difference between mFB and p-fluorobenzaldehyde is the appearance of a double-peak structure with 20—25 cm^{-1} each for the main bands in the former. The relative intensity between any pair of twin bands is almost independent of band mode, but very dependent upon how the crystals

Table 1. Wavenumbers and Assignments of the Main Bands in the Phosphorescence Spectra of mFB and mFB-α-d_1 in α-MCH at 4.2 K

mFB			mFB-α-d_1			
ν/cm^{-1}	$\Delta\,\nu/\mathrm{cm}^{-1}$	Rel. int.	ν/cm^{-1}	$\Delta\,\nu/\mathrm{cm}^{-1}$	Rel. int.	Assignment[a)]
24800	0	100	24852	0	100	0–0; 0_l
24778	22	47	24830	22	5	0–0; 0_h
24608	192	6	24679	173	5	$0_l-\nu_{25}$; k
			24657	195		$0_h-\nu_{25}$
23796	1004	5	23848	1004	5	$0_l-\nu_{18}$; m
23772	1028	3				$0_h-\nu_{18}$
23667	1133	15	23709	1143	12	$0_l-\nu_{16}$; n
23648	1152					$0_h-\nu_{16}$
23407	1393	4	23469	1383		$0_l-\nu_{11}$; u
23385	1415		23446	1406		$0_h-\nu_{11}$
23180	1620	13	23234	1618	12	$0_l-\nu_7$; p
23161	1639	5				$0_h-\nu_7$
23089	1711	40				Fermi. R[b)]
			23165	1687	20	$0_l-2\,\nu_{26}$
23079	1721	108	23148	1704	154	$0_l-\nu_6$; q
23056	1744	67	23126	1726	6	$0_h-\nu_6$
22793	2007	8				$0_l-2\,\nu_{26}$
22771	2029	3				$0_h-2\,\nu_{26}$

a) Given in Mulliken mode numbering. Designations are for Fig. 1b. b) A Fermi resonance band is suggested from its intensity. The detail is uncertain, however.

were made. These facts strongly suggest that there are two emitting species in the sample system. Two possibilities remain: (1) an intramolecular event and (2) an intermolecular event. For the latter, it is well known that MCH has two different phases, crystallographically, as mentioned in the experimental section. As described below, this type of crystallographic mixture gives a much greater splitting (i.e., 117 cm^{-1}). Although the possibility of other intermolecular events can not always be neglected, we here prefer event (1) to (2) due to the help of a favorable jet assignment by Y–E–I.[15] That is, we assume that the 22 cm^{-1} splitting is due to the two isomers, loc. cit.

Samples which underwent further annealing over a wide temperature range of 110—140 K usually contained a co-mixture of the both phases. For such samples, a new band system appears at the lower energy side by 117 cm^{-1}. The total spectra thus become more complex. The relative intensity ratio between the old and new band systems is very dependent on material purity, concentration, and annealing process. Two examples are shown in Fig. 2. The splitting value in mFB (22 cm^{-1}) is compared with the vapor value (30 cm^{-1}). The most notable thing, however, is that the relative intensity between the paired bands for the α-phase phosphorescence in the co-mixture crystals changes extremely compared to the spectrum of only a pure α-phase crystal (see Fig. 1b and Table 1) while an almost constant intensity ratio of $I(0_\mathrm{l})/I(0_\mathrm{h}) \approx 4$ is observed for the β-phase modification.[32] Paired ν_6 bands for both phase crystals appear in almost the same frequency spacing and intensity ratio as those of the origin bands. Other weak vibronic bands also reflect a similar band structure to that of the origin band region.

Phosphorescence spectrum of mFB-α-d_1 is shown in Fig. 2b. A crystalline splitting of 117 cm^{-1} and a small isomer splitting of 22 cm^{-1} are found again.[33] At a glance, it may be surprising that those splitting are the same within the experimental errors as the respective value of the undeuterated material, mFB. The small environmental effect on the deuteration shift, as has been observed for the $^3\mathrm{n}\pi^*$ state of benzaldehyde[26] in an α- and β-phase MCH crystals on going from benzaldehyde to benzaldehyde-α-d_1, may be one reason. Another might be that an environmental change effect on the rotational potential barrier of mFB is not major from α-phase to β-phase in the sense of the total sum of such effects for both the ground and the $^3\mathrm{n}\pi^*$ state.

For a comparison, $\mathrm{S}_1 \leftarrow \mathrm{S}_0$ phosphorescence excitation spectrum of mFB in an α-phase MCH matrix was examined together with its phosphorescence spectra (see Fig. 3). The arrowed bands in the two spectra, 0_l and 0_h, correspond to each other's origin bands as estimated from almost the same intensity ratio between the respective two bands:

$$[I(0_\mathrm{l})/I(0_\mathrm{h})]_\mathrm{phosphorescence} \approx [I(0_\mathrm{l})/I(0_\mathrm{h})]_\mathrm{phosphorescence\ excitation}.$$

From a simple assumption for state populations, each stronger band is taken to originate from the energetically stabler species of mFB in the ground state. For the $\mathrm{S}_1 \leftarrow \mathrm{S}_0$ transition, the order of the paired band is reversed and its separation amounts to 17 cm^{-1}.

Rotational Isomers in Vapor Phase. Since the total vapor pressure for the present experiments is determined almost by the partial pressure of the energy sensitizer, i.e., ca. 5 Torr benzene, mFB molecules in the excited triplet state with a radiative lifetime of ca. 10^{-3} second are distributed approximately according to the Boltzmann distribution rule.

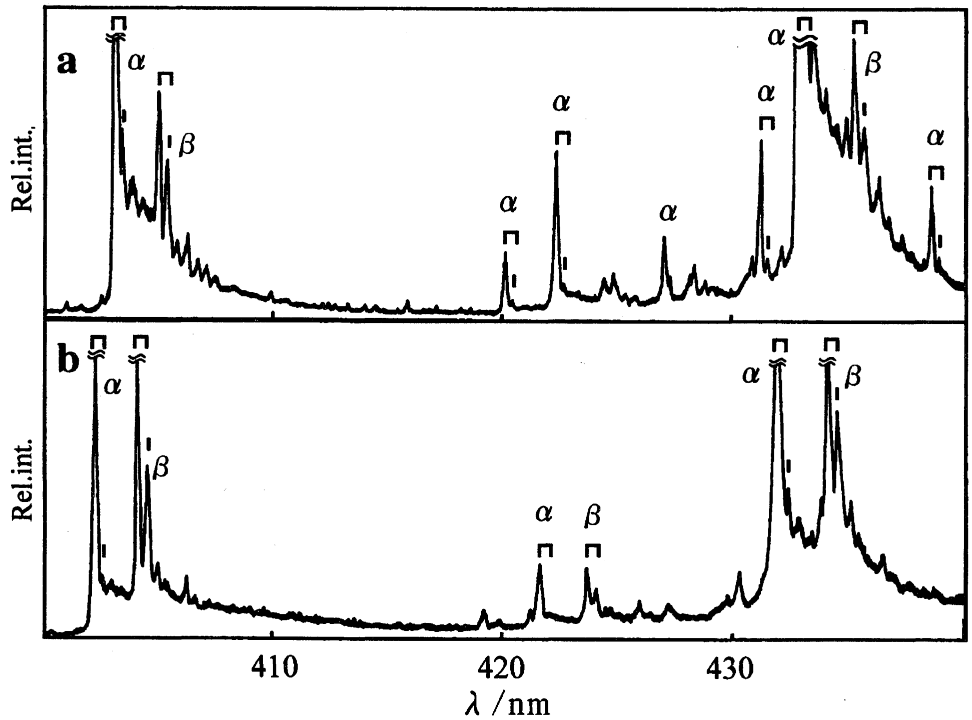

Fig. 2. Phosphorescence spectra of (a) mFB and (b) mFB-α-d_1 in MCH matrices at 4.2 K.

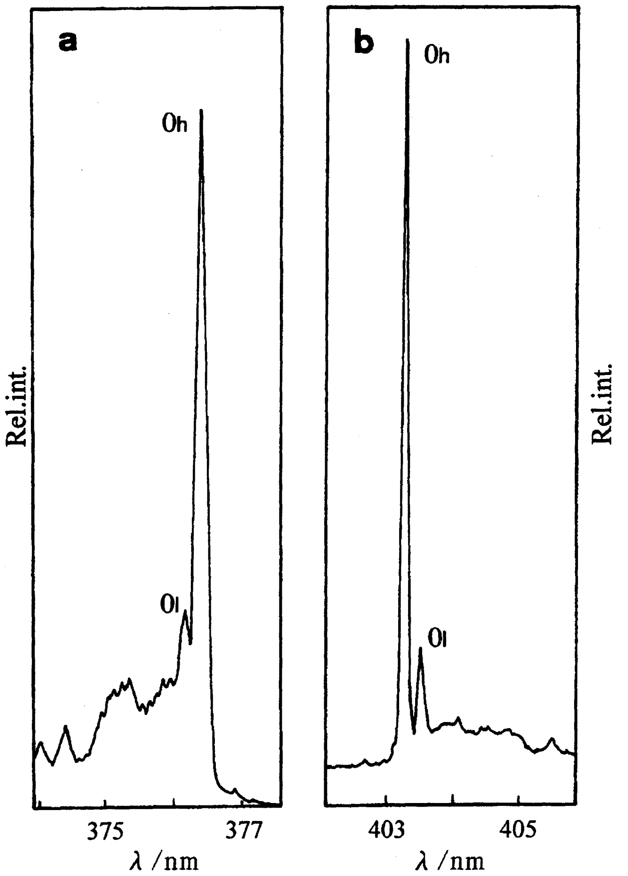

Fig. 3. (a) $S_1 \leftarrow S_0$ phosphorescence excitation and (b) $T_1 \rightarrow S_0$ phosphorescence spectra of mFB in an α-phase MCH matrix at 4.2 K (in part).

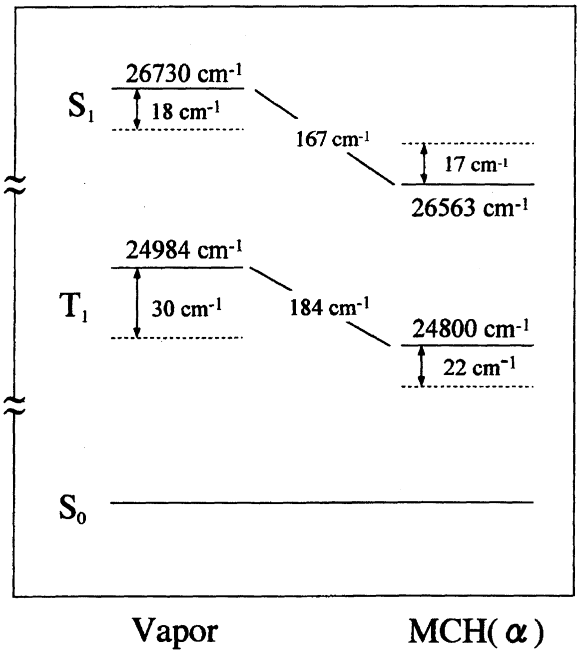

Fig. 4. Schematic energy level diagram for mFB in the vapor phase and in the α-phase MCH matrix. All energies are figured under an assumption of $E(S_0)=0$ for the both rotational isomers.

If the phosphorescence emission is due to only one of the two isomers (as was considered by H–T),[17] a simple estimation predicts that the Boltzmann populations of the two vibronic levels are: $P(0^0)/(35^1)=3$ at 300 K using $35^1=210$ cm^{-1}. The observed intensities of the twin bands, however, are almost the same. The 35_1^1 assignment by H–T for the red-side component of the twin is thus doubtful unless there are other special reasons. Thus, the Y–E–I conclusion may be to a great extent rationalized.

A single structure for the 26_1^1 band at -578 cm^{-1} is very indicative. A rough estimation of the tunneling rates of several internal rotational levels and an assumed enthalpy energy (ca. 200 cm^{-1}) are likely to support a single structure for the band. Finally, for a summary account a schematic diagram of the energy relationship between the two rotamers is given in Fig. 4.

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28) Band contours of the related two origin bands are different to each other. Here we take only the band heads. The intrinsic zero level is estimated at 2 cm^{-1} lower than the 0_0^0 head at 24984 cm^{-1} by H–T (Ref. 16). The corrected value is very close to that by Y–E–I (Ref. 15).

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32) Phenomenologically speaking, the molecular energies of guest molecules doped in α- and β-phase MCH crystals are not always stable at higher and lower temperatures than the phase transition temperature, respectively. Under a certain circumstance, a guest molecule embedded in *a stabler host framework* may be squeezed from such environmental molecules.

33) As the rotational isomer splitting, we observed 22 cm^{-1} for the α-phase spectrum of mFB-α-d_1 and 25 cm^{-1} for the β-phase one.