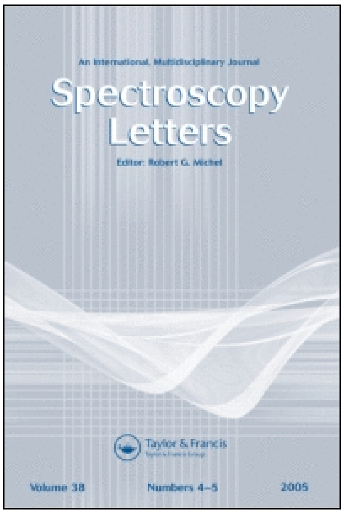

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Matrix Isolation Infrared Spectra of Methylacetate III. UV-Induced E photorotamerisation of Methylacetate in Argon Matrices

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MATRIX ISOLATION INFRARED SPECTRA OF METHYLACETATE.

III. UV-induced Z→E photorotamerization of methylacetate in argon matrices.

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ABSTRACT

Broadband UV-irradiation of methylacetate isolated in argon matrices causes rather strong modifications to appear in the IR spectrum. Evidence was obtained for a photochemical interconversion of the stable Z-conformer into the less stable E-conformer followed by photolytic decomposition of the latter into stable products. Most of these products could be identified from their IR absorptions. The reverse E→Z interconversion is a thermal process with an activation energy of about 10 $kJmole^{-1}$. A normal coordinate analysis based on a

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transferable valence force field obtained from the literature allowed to assign approximate IR frequencies of E-methylacetate.

INTRODUCTION

Photorotamerization refers to a process of conformer interconversion induced by UV or IR irradiation of polyatomic molecules. This process occurs quite frequently in solid low-temperature matrices where the extremely low thermal energy available prevents the photochemically formed, less stable conformer to relax fastly to the stable isomer. Since the first observation of photoisomerization for HONO in a N_2 matrix [1] , an extensive number of examples is known nowadays and excellent review papers have been published by Barnes [2], Perutz [3], and Frei and Pimentel [4]. When UV light is used to induce rotamerization the process is frequently accompanied by other photoprocesses such as photoelimination or photofragmentation [3].

The conformational problem of esters has been the subject of great interest for many years [5]. For methylacetate a heavy-atom planar "cis" (Z) conformation has been confirmed by investigations of dipole moments [6-9], electron diffraction patterns [10], infrared [11-13] and microwave spectra [14]. The presence of an equilibrium between Z and E rotamers has only been suggested from ultrasonic studies [15]. The first indication of rotational isomerism of methylacetate in matrices has been found by Blom and Günthard who trapped thermal molecular beams in Ar and tentatively assigned a very weak IR absorption at 1784 cm^{-1} to the $\nu_{C=O}$ vibration of the E conformer [16]. These authors estimated a ΔH (E-Z) value of 35.6 $kJmol^{-1}$. More recently Wiberg and Laidig have quoted a ΔH value of 43.55 $kJmol^{-1}$ and an energy barrier of 13.35 $kJmol^{-1}$

as the result of detailed ab initio calculations [17]. In 1983 Müller, Hollenstein and Huber have reported UV-induced Z→E isomerization followed by photolytic decomposition of the E rotamer for methylformate [18]. Using a transferable valence force field approach a complete frequency assignment was obtained for the unstable E isomer.

In the present work we demonstrate that a UV Z→E photorotamerization process occurs in matrix isolated methylacetate.

EXPERIMENTAL

The matrix techniques and apparatus used in this work were the same as those described in earlier papers [19,20] except for the fact that the cryostat was furnished with a quartz window allowing UV-irradiation of the sample. The matrix-to-solute ratio was kept constant at 1000 ± 50. The sample temperature was maintained at 12 K during deposition and between 12 and 14 K during photolysis and scanning.

The photochemical experiments were carried out with a 125 W-high pressure OSRAM HQL lamp and spectra were scanned with Perkin Elmer 180 and 580B spectrophotometers.

RESULTS AND DISCUSSION

1. UV-induced IR absorptions

The IR spectrum of methylacetate (MeAc) in Ar matrices has been described in detail in earlier papers of this series [20,21]. The spectrum is consistent with the presence of only 1 conformer, the Z- or "cis"-conformer [11], and trapping at 12 K in Ar does not disturb the overwhelming excess of the Z-form from the gas phase.

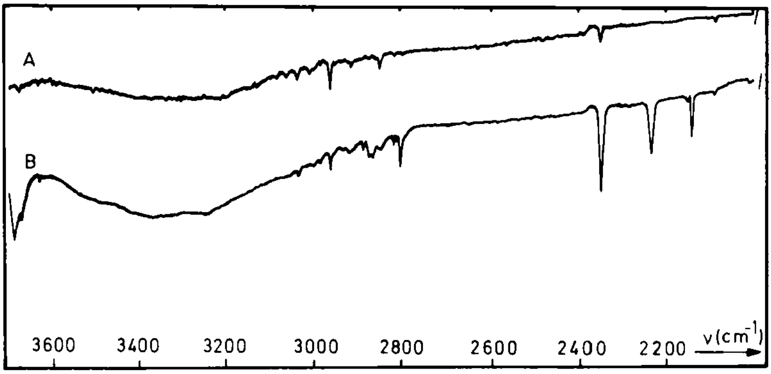
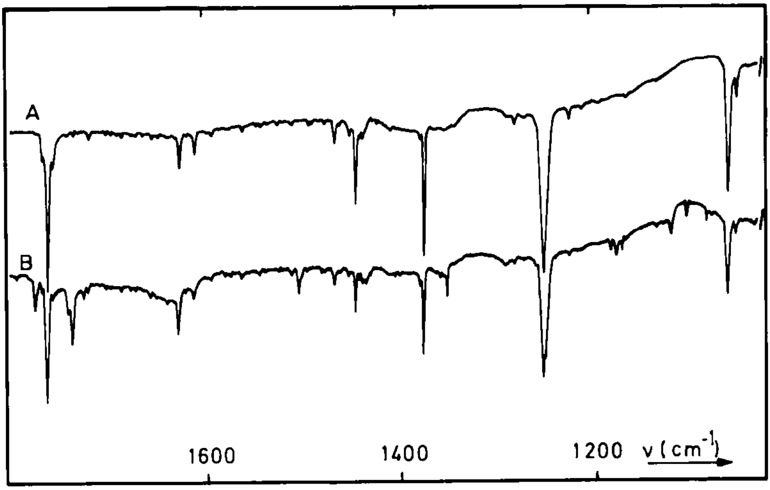


FIG. 1 The IR spectrum of MeAc in Ar (M/S = 1000) at 12 K. A : before UV-irradiation; B : after 4 hr UV-irradiation.

Figure 1 displays the spectral changes induced by a 2 hr UV irradiation of a 1:1000 MeAc/Ar matrix. Under these experimental conditions many new absorptions appear although most are relatively weak. Table 1 summarizes the spectral data obtained here. Some of the induced bands are close to Z-MeAc absorptions, e.g. the 1774 cm^{-1} feature is not far from the $\nu_{C=O}$ at 1761 cm^{-1}, but others appear in spectral regions which are almost transparant initially (e.g. 2600-2000 cm^{-1}).

Furthermore, different intensity decreases are observed for different initial absorptions of the starting material. As an illustration, for the 2 hr irradiated sample of fig. 1, the $\nu_{C=O}$ band (1761 cm^{-1}) looses about 40% of its original intensity whereas the δ_{CH_3-C} band (1370 cm^{-1}) only decreases by about 20%. All these observations suggest the photochemical formation of different absorbing species some of which closely resemble the original molecule. Conformer interconversion is one of the phenomena consistent with a selective frequency perturbation of a polyatomic molecule.



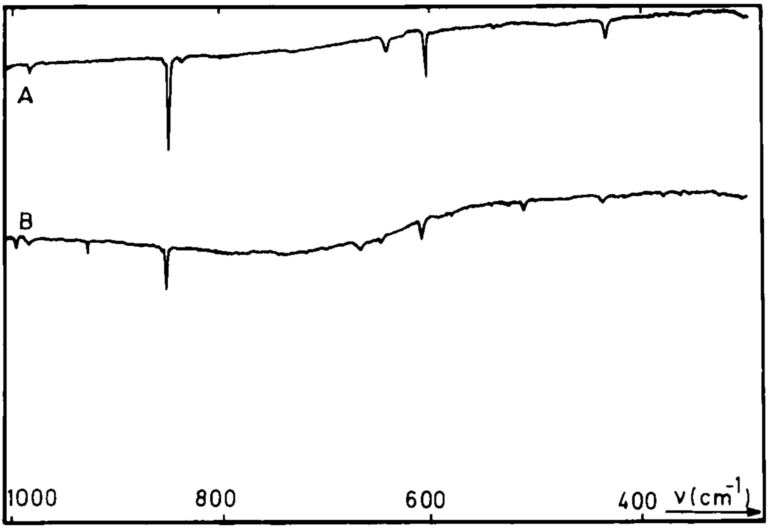


FIG. 1 Continued.

TABLE 1

Experimental IR Absorptions of CH_3COOCH_3 in Ar after UV-Irradiation at 12 K

Experimental frequency (cm^{-1})	Assignment for Z-conformer (a) [11,20]	Type of induced band (see text)
3684-3670		II
3600-3100 broad	(b)	
3035	ν_{CH_3}	
3007	ν_{CH_3}	
2965	ν_{CH_3-O}	
2952	ν_{CH_3-C}	
2920	ν_{CH_3}	
2888		II
2876		II
2850	2 x 1441	
2818		II
2810		II
2347		II
2233		II
2150	water complex with CO [18]	
2141-2138		II
2085	2 x 1057	
1794		?
1774		I
1761	$\nu_{C=O}$	
1756	dimer	
1749-1740	water complex 21	
1736		II
1719	$\nu^{13}_{C=O}$	
1499		II
1462	δ_{CH_3-O}	
1459		I
1447	δ_{CH_3-O}	
1441	δ_{CH_3-O}	
1434	δ_{CH_3-C}	
1431		II
1425		II

TABLE 1 (cont.)

Experimental frequency (cm^{-1})	Assignment for Z-conformer (a) [11,20]	Type of induced band (see text)
1375	dimer	
1370	$^{\delta}CH_3$-C	
1353		
1346		II
1278	2 x 642	
1266	water complex [21]	
1255	dimer (c)	I?(c)
1246	$^{\nu}$C-O	
1244		II
1220	$^{\rho}CH_3$-O	
1190	$^{\rho}CH_3$-O	
1179		I
1173		II
1166		II
1160	$^{\rho}CH_3$-C	
1116		I
1098		II
1080-1074		II
1057	$^{\nu}$O-CH_3	
1030		II
991		II
980	$^{\rho}CH_3$-C	
924		II
851	dimer	
848	$^{\nu}$C-C	
662		II
642	$^{\gamma}CH_3COO$	
603	$^{\delta}$OCO	
575		II
509		I
434	$^{\delta}$CCO	

(a) ν = stretching, δ = deformation, ρ = rocking, γ = out of plane mode.

(b) absorption due to H_2O on CsI-window and/or H-bonding with CH_3OH

(c) overlap of weak dimer ν_{C-O} band with an induced band of type I

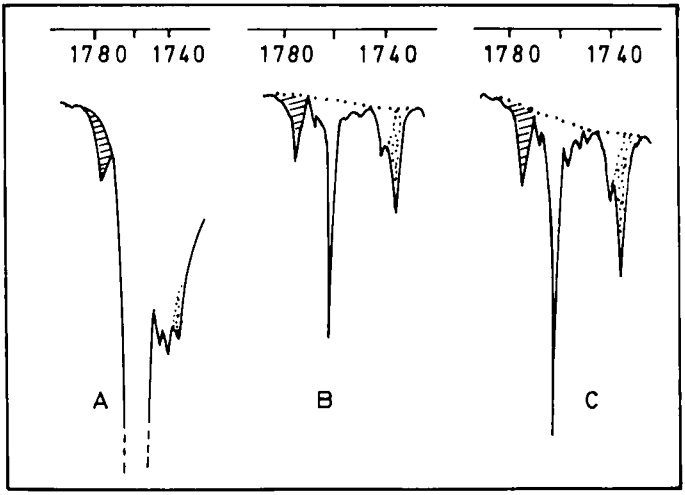


FIG. 2 Variation of the intensity of UV-induced absorptions in the spectral region 1800–1700 cm^{-1} of MeAc (M/S = 1000). A = 30'; B = 120'; C = 240'.

Additional experimental evidence was obtained by variation of irradiation time and matrix temperature. The spectral region 1800-1700 cm^{-1} was selected for this purpose.

Figure 2 shows the effect of variation of the time of irradiation and of the distance UV-lamp-to-matrix sample. In the early stages of the process both the new bands at 1774 and 1736 cm^{-1} appear in the spectra. Prolonged irradiation leads to a preferential increase of the 1736 cm^{-1} feature in contrast to the high frequency band which remains more or less constant. A larger irradiation distance slows down the appearance of both new absorptions.

Relative intensity values in this spectral region are summarized in Table 2. The results show that 2 different types of induced absorptions are present in

TABLE 2

Relative Intensities of MeAc IR Absorptions (1800-1700 cm^{-1}) as a Function of UV-Irradiation Time and Ar Matrix Temperature (M/S = 1000/1)

Time of UV-irradiation (min) or temperature (°K)	$\frac{I_{1774}}{I_{1761}}$	$\frac{I_{1736}}{I_{1761}}$	$\frac{I_{1774}}{I_{1736}}$
t = 30	(a)	(a)	1
60	0.21	0.32	0.64
120	0.24	0.57	0.42
240(b)	0.13	0.30	0.43
T = 10	0.31	0.68	0.46
35	0.29	0.62	0.47
38	0.09	0.44(c)	0.21(c)

(a) too weak to be accurately measured.

(b) a 2x greater distance UV-lamp - sample holder was used in this experiment

(c) approximate value due to low frequency broadening of 1736 cm^{-1} band.

the spectra : type I which appears from the early stages of irradiation and type II which grows during the later stages, mostly at the expense of the former type.

A similar spectral intensity analysis performed in the other regions of the matrix spectra allowed to identify at least 5 bands as being of type I :

1774 cm^{-1}, 1459 cm^{-1}, 1179 cm^{-1}, 1116 cm^{-1}, 509 cm^{-1}

Some puzzling intensity differences were observed for a few type II absorptions in the region 2400-2100 cm^{-1}. These observations will be discussed below.

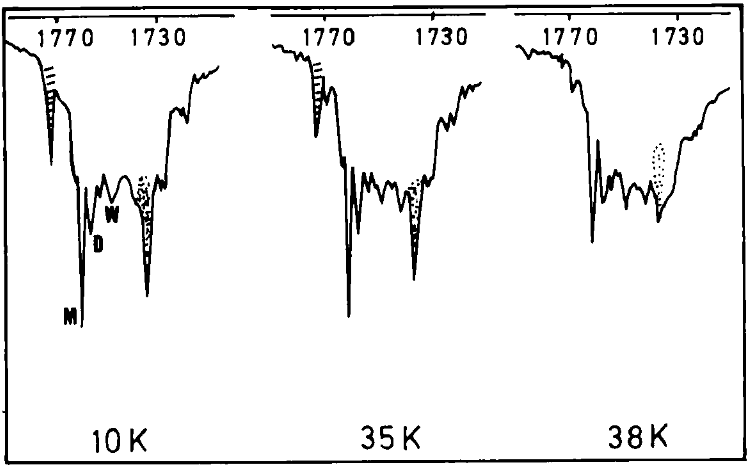


FIG. 3 Influence of the matrix temperature on UV-induced absorptions in the spectral region 1800–1700 cm^{-1} of MeAc/Ar (M/S = 1000, irradiation time = 150').

The spectral modifications induced by temperature variation of the matrix samples are illustrated in Figure 3 ($\nu_{C=O}$ region). After each temperature increase the sample was recooled to 12 K and the IR spectrum was scanned. Apart from an intensity enhancement of features due to self-association [20] or association with water impurities [21] no detectable differences are observed for the type I 1774 cm^{-1} and the type II 1736 cm^{-1} bands within the temperature range 12-35 K. In the range 35-38 K however the band at 1774 cm^{-1} almost disappears in contrast to the type II band at 1736 cm^{-1}. The latter exhibits low frequency broadening which is most probably due to self-association of the species absorbing at 1736 cm^{-1}. Relative intensities measured at different matrix temperatures are included in Table 2. Similar results are obtained in other spectral regions, e.g. 509 cm^{-1} behaves like 1774 cm^{-1} (type I) and 1431 cm^{-1} like 1736 cm^{-1} (type II).

The whole set of experimental results shows that 2 types of induced absorptions appear in the spectra of irradiated samples : those of type I which appear from the early stages and disappear between 35 and 38 K, and those of type II which grow in during later stages and persist after temperature cycling.

2. Identification of photolysis products (type II bands)

The observation of different types of induced bands is consistent with earlier results for methylformate [18]. After photorotamerization Z→E the latter form was photolyzed to different products such as CO + CH_3OH, CH_3COOH, or CO_2 + CH_4. If one assumes the same photolysis reaction paths to occur in CH_3COOCH_3, one expects to observe CO + CH_3OCH_3, and CO_2 + C_2H_6 absorptions in the IR spectra. A comparison of the frequencies of experimental type II absorptions with literature frequencies for CO, CO_2 and $(CH_3)_2O$ in Ar matrices leads to a positive identification of these molecules as photolysis fragmentation products :

CO/Ar : 2137 cm^{-1} [22]

CO_2/Ar : 2347, 662 cm^{-1} [23]

$(CH_3)_2O$/Ar : 2890, 2869, 2821, 1427, 1244, 1172, 1098, 926 cm^{-1} [24]

No clear C_2H_6-band was observed in the spectra. The same problem was encountered for CH_4 in the earlier paper on methylformate [18], and also by Blom and Günthard for C_2H_6 in their study on methylacetate [16]. To our opinion it does not rule out C_2H_6 as a photofragment, since alkanes are characterized by rather weak absorptions in the regions 2900, 1500-1400 and 850-800 cm^{-1} [25], and the weak C_2H_6 features might overlap with other bands in these regions. Further photolysis products must be present in the matrices, because a number of other type II absorptions remain to be identified. In the work of Blom and Günthard, the following thermal decomposition schemes of methylacetate were proposed to explain part of the thermally formed and subsequently trapped species [16] :

$$CH_3COOCH_3 \longrightarrow C_2H_6 + CO_2$$
$$CH_3COOCH_3 \longrightarrow CH_4 + H_2CO + CO$$
$$CH_3COOCH_3 \longrightarrow CH_3OH + CH_2CO$$

Apart from the products C_2H_6, CO_2 and CO already discussed, H_2CO and CH_3OH are positively identified in the list of type II bands in our spectra :

H_2CO/N_2 : 2877, 2810, 1733, 1498, 1245, 1172 cm^{-1} [26]
CH_3OH/Ar : 3667, 1335, 1160? 1077, 1034 cm^{-1} [27]

The identification of CH_2CO (ketene) is doubtful, although the 2141 cm^{-1} splitting on the CO absorption band corresponds well with the literature frequency of ν_2(CO) in ketene, as does the 1116 cm^{-1} band (this band is of type I however) with the literature ν_4 frequency [28]. The rather strong photolysis band at 2233 cm^{-1} is not assigned so far. The frequency is not far from the literature $\nu_{C=O}$ value for structures C=C=C=O which also absorb at 579 cm^{-1} [29]. It might be possible that ketene is formed in a primary photolysis stage and that this product is further transformed in subsequent photoreaction steps. This could also explain the rather

TABLE 3

Comparison of Z→E Frequencies and Shifts (cm^{-1}) for Methylformate and Methylacetate in Ar Matrices.

Vibrational mode	Methylformate [18]			Methylacetate (this work)		
	Z	E	Δν	Z	E	Δν
$\nu_{C=O}$ (a')	1745	1777	+32	1761	1774	+13
δ_{CH_3-O} (a')	1459	1483	+24	1462	?	?
δ_{CH_3-O} (a")	1446	1467	+21	1447	1459	+12
δ_{CH_3-O} (a')	1433	1464	+31	1441	1459	+18
ν_{C-O} (a')	1205	1239	+34	1246	1255	+9
δ_{CH_3-O} (a')	1161	1099	-62	1220	1179	-41
ν_{O-CH_3} (a')	921	1017	+96	1057	1116	+59
δ_{OCO} (a')	767	635	-132	603	509	-94
δ_{CCO} (a')	308	372	+64	434	509	+75

puzzling intensity variation in the region 2400-2100 cm^{-1} mentioned earlier.

3. The E-rotamer of methylacetate (type I bands)

A first indication that the UV induced type I absorptions of MeAc are in fact fingerprints of the E conformer follows from the comparison with Z and E methylformate presented in Table 3. This comparison has been limited to vibrational modes within the identical $COOCH_3$ subunit in the 2 ester molecules. The interpretation of the 5 type I absorptions of MeAc (and of the 1255 cm^{-1} induced shoulder) in terms of shifted $COOCH_3$ modes in the E conformer leads to a qualitative similarity with the methylformate conformational shifts.

These assignments are further supported by a normal coordinate calculation using force constants transferred from the Z conformer, whose constraint valence force field has been determined by Hollenstein and Günthard [30]. In a first step the frequencies of the Z conformer were computed using the gas-phase equilibrium geometry from the literature [10,31,32] and the transferable valence force field from the paper of Hollenstein and Günthard [30]. The fit between calculated and experimental frequencies which are given in Table 4 is very satisfactory. In a subsequent step the whole set of force constants was transferred to the E-conformer. Although transfer of diagonal constants is not allowed by the transfer rules [30], this procedure can be used as a first approximation to predict frequency shifts due to conformer interconversion. The procedure is justified by the results for methylformate for which Z and E force constants have been adjusted by iterative procedures. As a matter of fact only the COC-bend and C_e-O torsion diagonal constants showed differences outside the range 1-4% [18]. Inspection of table 4 shows that significant shifts are predicted for 9 vibrational modes of the E conformer. Because of the direct transfer of force constants these shifts only reflect the G-matrix or conformer geometry effect. The qualitative agreement between predicted frequency shifts and experimental shifts of type I absorptions (Table 4) strongly supports the idea of formation of the E conformer in the irradiated matrices.

A semi-quantitative picture of the Z-E energy diagram can be obtained from figure 4. Using the relation between temperature and energy barrier of conformer interconversion published by Barnes [2] a E→Z barrier of 9-11 $kJmol^{-1}$ can be estimated from the temperature variation experiments. This value order agrees reaso-

TABLE 4

Fit between Gas Phase Experimental and Calculated IR Frequencies using a Same Force Field for Z and E Methylacetate. Comparison with Experimental Z-E Frequency Shifts. (cm^{-1})

Fundamental	Exp. [30]	Calc. Z MeAc	Δ	Calc. E MeAc	Δ	Exp. Z→E shift in Ar
ν_{CH_3-C}	3054	3054	0	3054	0	
ν_{CH_3-O}	3046	3046	0	3046	0	
ν_{CH_3-O}	3013	3013	0	3013	0	
ν_{CH_3-C}	2995	2995	0	2994	- 1	
ν_{CH_3-O}	2967	2968	1	2968	1	
ν_{CH_3-C}	2940	2940	0	2940	0	
$\nu_{C=O}$	1769	1769	0	1789	20	13
δ_{CH_3-O}	1473	1474	1	1474	1	
δ_{CH_3-O}	1470	1471	1	1470	0	
δ_{CH_3-O}	1443	1443	0	1447	4	12
δ_{CH_3-C}	1440	1439	- 1	1439	- 1	
δ_{CH_3-C}	1436	1436	- 1	1435	- 1	
δ_{CH_3-C}	1374	1373	1	1370	- 4	
ν_{C-O}	1250	1250	0	1269	+ 19	9
ρ_{CH_3-O}	1191	1192	1	1151	- 40	-41
ρ_{CH_3-O}	1166	1167	1	1165	- 1	
ν_{O-C}	1053	1053	0	1051	- 2	
ρ_{CH_3-C}	1053	1052	1	935	- 118	?
ρ_{CH_3-C}	977	976	1	975	- 2	
ν_{C-C}	847	847	0	845	- 2	
δ_{OCO}	636	637	1	591	- 45	-28
γ_{CH_3COO}	599	600	1	662	+ 63	20(b)
δ_{CCO}	436	437	1	519	+ 83	75
δ_{COC}	296	297	1	268	- 28	(a)
τ_{CO}	185	186	1	197	12	(a)
τ_{OCH_3}	136	136	0	136	0	
τ_{CCH_3}	73	73	0	71	- 2	
Sum of deviation			16		377	

(a) experimental frequencies not studied in this work.

(b) this result shows that a shifted band overlaps with the CO_2 photoproduct absorption at 662 cm^{-1}.

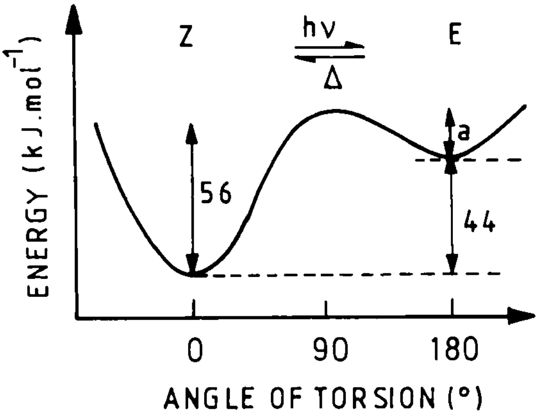


FIG. 4 Schematic energy diagram of Z⇆E interconversion of MeAc in Ar (Z→E barrier and ΔH_{Z-E} from ref. 17; a = 9–11 kJmol^{-1}).

nably well with the difference between calculated values of ΔH_{E-Z} (44 kJmol^{-1}) and energy barrier Z→E (≈ 56 kJmol^{-1}) [17].

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