zones such as those in Figure 8,[69] and that there may be "separatrix states" whose phase space density is localized in the vicinity of the broken D,E/F or F/G separatrices.[69]

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Infrared Photodissociation of Hydrogen-Bonded Complexes Trapped in Inert Matrices. The Ethylene Oxide–Hydrogen Iodide System

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Matrix isolation infrared spectroscopy applied to the ethylene oxide/H(D)I system trapped in solid Ar and N_2 allows identification of several kinds of hydrogen-bonded complexes: a 1:1 species which exists under two different structures and larger aggregates giving rise to proton transfer with formation of ionic species of the type $[(EO)_2H]^+$ or $(IHI)^-$ characterized by quasi-symmetrical single-minimum potential functions for the proton (proton sharing). The interconversion between the hydrogen-bonded (C) and the non-hydrogen-bonded (U) forms of the 1:1 complex is seen to depend on two parameters: temperature and infrared irradiation. Kinetic measurements of the disappearance (or appearance) of C have shown that the C → U conversion is mainly induced by IR radiations in the range 1500–2300 cm^{-1}, corresponding to the excitation of ν_s (HI stretching mode), while the C ← U transformation is thermally induced above 17 K. From the temperature dependence of the kinetic rate constant an activation energy for C ← U conversion has been obtained. The effect of HI/DI isotopic substitution is also discussed. The very slow C → U conversion rate with DI suggests a barrier greater than 1500 cm^{-1} for this photoprocess.

Introduction

In two recent papers,[1,2] hereafter referred to as 1 and 2, we have described the photodissociation of the hydrogen-bonded $CH_3CN{:}HI$ complex (C) trapped in nitrogen and in argon. Three main observations were made in these experiments: (i) photodissociation occurs upon irradiation in the mid-IR; (ii) it also occurs in the dark, because of the infrared emission from the envelope and the entrance windows of the cryostat; (iii) temperature increase of the matrix from 10 to 20 K allows the regeneration of C in the absence of any migration of the molecules within the matrix host crystal. These observations are explained in terms of interconversion between the hydrogen-bonded (C) and the non-hydrogen-bonded (U) forms of the CH_3CN/HI pairs, the stable one being C:

$$\mathrm{C} \underset{T}{\overset{h\nu}{\rightleftarrows}} \mathrm{U}$$

Other photodissociation processes of hydrogen-bonded B:HI complexes by infrared radiations have been evidenced in this laboratory, and it is the purpose of this paper to describe in detail the results obtained for B = ethylene oxide (EO) which have been outlined in a previous publication.[3] In short, deposition of EO/HI/Ar mixtures allows the identification of complexes with various stoichiometries. The 1:1 species, mainly characterized by a broad band centered at 1950 cm^{-1} assigned to the HI stretching mode (ν_s), is seen to be very sensitive to infrared irradiation; indeed, it totally disappears in 20 min when exposed to the full light of the spectrometer light source of a matrix temperature lower than 17 K. But it reappears upon temperature increase below the annealing limit (see Fig. 8 of ref 3).

Extensive experiments in Ar and N_2 matrices have been carried out in order to obtain the most complete information about the infrared photochemistry involved in the H-bond breaking. They will be reported in the second section of this paper, the first one being devoted to the description of the spectra of $(EO)_m(HI)_n$ (or $m{:}n$) complexes, with special care to identify the modes of complexed EO that were not considered in ref 3.

Experimental Section

The apparatus and sampling conditions were identical with those used earlier in this laboratory.[4] Experiments were conducted in the twin-jet mode, the two dopants being codeposited from separate inlets on a CsI window maintained at 20 K for Ar and 17 K for N_2 matrices, at a deposition rate of 10 mmol/h. Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer. The light emitted by the source was used for photodissociation experiments. As shown in paper 2, the illumination of a unit area of the sample in the range $(\nu, \nu + \Delta\nu)$ is

$$E(\nu) = 6 \times 10^{-3}\beta(\nu)[0.66L_{1590}(\nu) + 0.33L_{1440}(\nu)]\Delta\nu$$

where $L_T(\nu)$ is the radiance of the blackbody at frequency ν and temperature T and $\beta(\nu)$ the emittance of the source. β equals 0.9 for $\nu < 1900$ cm^{-1} and 0.3 for $\nu > 2700$ cm^{-1} and varies linearly within this frequency range. In dark process experiments, the sample illumination $E_{DP}(\nu)$ is supposed to arise from the laboratory thermal bath through the two entrance windows of the cryostat, leading to

$$E_{DP}(\nu) = 2\Omega L_{295}(\nu)\Delta\nu$$

where Ω is the solid angle of irradiation of the sample.

HI (Matheson) and natural ethylene oxide (EO-h_4, Merck-Schuchardt, 99% purity) were distilled from trap to trap at low temperature. DI was prepared by action of phosphorus on iodine in the presence of D_2O (CEA, 99% isotopic enrichment) for 12 h in the dark. C_2D_4O (EO-d_4) was prepared in three steps, according to the method proposed by Leitch and Morse:[5] (i)

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[2] Schriver, L.; Schriver, A.; Racine, S.; Perchard, J.-P. *Chem. Phys.* **1988**, *119*, 95.

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[5] Leitch, S.; Morse, A. T. *Can. J. Chem.* **1952**, *30*, 924.

TABLE I: Frequencies (cm^{-1}) and Assignment of the Infrared-Active Modes of Monomeric Ethylene Oxide ($(CH_2)_2O$ and $(CD_2)_2O$) Trapped in Solid Argon and Nitrogen[a]

		Ar		N_2	
symmetry	vibrational mode	EO-h_4	EO-d_4	EO-h_4	EO-d_4
A_1	ν_1 CH_2 stretching	3009.5 (0.3)	2213 (0.4)	3007 (0.14)	2210.5 (0.5)
			1313.5 (0.i)		1310.5 (0.4)
	ν_2 CH_2 bending	1496 (0.01)	1312.5 (0.15)	1493.5 (0.01)	1308 (0.15)
			1311 (0.1)		1307 (0.1)
	ν_3 ring breath	1272.5 (0.3)	1014 (0.2)	1272 (0.35)	1015 (0.2)
			1013 (0.15)		
	ν_4 CH_2 wagging	1125.5 (0.03)	966 (1)	1124.5 (0.02)	964 (0.96)
					958.5 (0.7)
					759 (0.65)
	ν_5 ring bending	879 (1)	758 (0.6)	875 (1)	757 (0.65)
		877 (0.6)	755 (0.6)		755.5 (1)
A_2	ν_6 CH_2 stretching	3065.5 (0.02)		3063 (0.02)	
	ν_7 CH_2 twisting		940 (0.08)		940 (0.05)
	ν_8 CH_2 rocking		706.5 (<0.01)		701 (0.01)
			702.5 (<0.01)		
B_1	ν_9 CH_2 stretching	3020 (0.1)	2181 (0.8)		
			2177 (0.9)	3017 (0.06)	2182 (0.24)
			2176.5 (0.2)		2179.5 (0.48)
	ν_{10} CH_2 bending	1470 (0.02)	1131 (0.1)	1467.5 (0.02)	1127.5 (0.08)
	ν_{11} CH_2 wagging	1154 (0.06)	956.5 (0.25)	1152.5 (0.12)	954 (0.42)
	ν_{12} ring bending	821.5 (0.4)	810.5 (0.3)	822 (0.06)	806.5 (0.54)
		817 (0.35)	806 (0.2)	816.5 (0.2)	
B_2	ν_{13} CH_2 stretching	3076.5 (0.4)	2325 (0.8)	3076 (0.2)	2325.5 (0.5)
					2322.5 (0.25)
	ν_{14} CH_2 twisting	1148 (0.01)	900 (0.1)	1144 (0.01)	900.5 (0.2)
			898 (0.2)		898 (0.4)
	ν_{15} CH_2 rocking	812 (0.1)	586 (0.05)	813.5 (0.08)	586.5 (0.16)
				811 (0.08)	

[a] The relative absorbances are reported in parentheses.

TABLE II: IR Frequencies (cm^{-1}) of HI and DI Engaged in Complexes with EO-h_4 and EO-d_4 As Measured in Argon and Nitrogen Matrices and Assignment

Ar matrix				N_2 matrix				
EO-h_4		EO-d_4		EO-h_4		EO-d_4		
HI	DI	HI	DI	HI	DI	HI	DI	assignment
2108 (6)	1515 (4)		1515 (4)					H(D)I end of chain in $m:n$ aggregates ($n > m$)
	1506 (4)		1506 (4)					
	1466 (6)		1465 (15)		1448 (15)		1455 (15)[a]	DI polymer in $m:n$ aggregates ($n > m$)
							1440 (15)[a]	
2020 (130)	1445 br	2045	~1440 br	2020 br	1430 br	2040 br	1425 sh	H(D)I interacting with ions (HI) or belonging to $m:n$ aggregates ($m > n$) (DI)
			1439 sh					
1950 (180)[a]	1397 (25)[a]	1945 (150)[a]	1411 (50)[a]	1950 (140)[a]	1390 (45)[a]	1950 (170)[a]	1408 (60)[a]	1:1, ν_s
			1395 (50)[a]				1388 (60)[a]	
				1870 br				1:n, HI perturbed by EO and HI
1500–800				1500–800				$(BHB)^+$, $(IHI)^-$ asym structure
660 (40)				660 (30)		650 (50)		$(BHB)^+$ sym structure
650 (50)								$(IHI)^-$ sym?
390 (6)		391 (6)						1:1, ν_l

[a] This band decreases in intensity upon IR irradiation.

reduction of 1,2-dibromoethane-d_4 to ethylene (C_2D_4) by zinc powder; (ii) addition of chlorine to C_2D_4 at 0 °C in presence of a large excess of water, leading to 2-chloroethanol-d_4; (iii) reaction of this alcohol on calcium hydroxide at 90 °C leading to EO-d_4. The isotopic enrichment is that of the dibromoethane-d_4 precursor (CEA 98% D). Finally, argon and nitrogen (Air Liquide, N50 purity) for matrices were used without further purification.

Spectral Data

1. EO/Ar or N_2. Infrared spectra of ethylene oxide ($(CH_2)_2O$ and $(CD_2)_2O$) in argon and nitrogen matrices were recorded. The observed bands, assigned on the basis of the normal-coordinate analysis of Nakanaga,[6] are listed in Table I. These data agree quite well with those reported by Le Brumant for EO trapped in argon.[7] There is one change with respect to the assignments proposed in ref 6, relating to the CD_2 wagging (B_1) localized here at 956 cm^{-1} instead of 900 cm^{-1}. This modification suggested by the data on complexed EO-d_4 will be discussed below.

2. EO/HI/Ar. At high dilution in HI and variable concentration in EO-h_4 the spectrum recorded immediately after deposition at 23 K in the dark displays two bands at 1950 and 390 cm^{-1} typical of hydrogen-bonded HI (Table II). The first one is strong and broad (full width at half-maximum (fwhm) = 180 cm^{-1}) and the second is weak and narrow (fwhm = 6 cm^{-1}). On the basis of concentration effects, these two bands are respectively assigned to the stretching, ν_s, and librational, ν_l, modes of hydrogen-bonded HI in the 1:1 complex (hereafter referred to as C). After exposure for a few minutes to the unfiltered beam of the spectrometer, the matrix temperature being maintained at 9 K, these bands strongly decreased in intensity (Figure 1). Warming the matrix to 23–25 K for 5 min reversed the process, leading essentially to the original spectrum. Replacing EO-h_4 by EO-d_4 led to the same observation, ν_s and ν_l being respectively measured at 1945 and 391 cm^{-1}. The intensity decrease of ν_s upon

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[6] Nakanaga, T. *J. Chem. Phys.* **1980**, *73*, 5451.

[7] Le Brumant, J. Thèse de doctorat es sciences, Université Pierre et Marie Curie, Paris, 1974.

TABLE III: IR Frequencies and Frequency Shifts with Respect to Monomer (in Parentheses) for Some Modes of EO-h_4 and EO-d_4 Engaged in the C and U Forms of the 1:1 Complex with HI or DI

		EO-h_4				EO-d_4			
		Ar		N_2		Ar		N_2	
		C	U	C	U	C	U	C	U
HI	ν_2	1489.5 (−6.5)		1491 (−2.5)		1305 (−8)	1309.5 (−3.5)	1303.5 (−5.5)	
	ν_{10}	1466.5 (−3.5)	1467 (−3)						
	ν_4	1123 (−2.5)				951.5 (−14.5)	960 (−6)	949 (−12)	959 (−2)
	ν_{11}					944 (−12.5)	954.5 (−2)		
	ν_5	868.5 (−9.5)		865.5 (−9.5)		759.5 (+3)			
	ν_{12}	801.5 (−17.5)		797.5 (−21.5)		791.5 (−16.5)	801 (−7)	787 (−19.5)	
DI	ν_2					1303 (−10)	1309 (−4)	1301 (−8)	1308 (−1)
	ν_{10}	1466 (−4)							
	ν_4	1122.5 (−3)		1121.5 (−3)		950.5 (−15.5)	960 (−6)	948.5 (−12.5)	958.5 (−2.5)
	ν_{11}					942.5 (−14)	953.5 (−3)	941 (−13)	951.5 (−2.5)
	ν_5			865.5 (9.5)		759.5 (+3)		759.5 (+2.5)	
	ν_{12}	801 (−18)		797 (−22)		791 (−17)	801 (−7)	787.5 (−19)	801

irradiation was not clearly counterbalanced by the appearance of a new band in the same spectral domain. We suggest that the HI mode of the new species U is probably located very close to the monomer line, in the absence of hydrogen bonding between the two partners HI and EO. The same situation was shown to occur in the case of the U form of the CH_3CN:HI complex, whose HI stretching mode was found at the frequency of monomeric HI in solid nitrogen but was not identified in argon matrices. Careful observations in the EO absorption domains allow the identification of complexed EO bands assignable to C on the basis of their behavior upon infrared irradiation. For EO-h_4 five modes are seen to be sensitive to complexation (Table III): ν_2, ν_{10} (CH_2 bending modes), ν_4 (CH_2 wagging), and ν_5 and ν_{12} (ring deformation). In all cases the bands are red-shifted with respect to that of monomeric EO-h_4, the largest shifts being observed for the ring modes ν_5 and ν_{12}. All these bands vanish upon infrared irradiation. Unfortunately, it is difficult to identify new bands belonging to the transformation product of C. Surprisingly, the situation is more favorable for EO-d_4 engaged in the same complex with HI. Indeed, in the absence of irradiation, five lines due to complexed EO-d_4 are assigned to C; upon irradiation these bands vanish, with concomitant appearance of four features in the same spectral regions (Table III). In the ν_2 region (at about 1312 cm^{-1} for monomeric EO-d_4) the absorption at 1305 cm^{-1} due to C is replaced by another one at 1309.5 cm^{-1}; the CD_2 wagging modes ν_4 and ν_{11} (respectively at 966 and 956.5 cm^{-1} for the monomer) are measured at 951.5 and 944 cm^{-1} for C, these two bands decreasing in intensity upon irradiation and being replaced by weaker features at 960 and 954.5 cm^{-1}. Finally, the ring deformations ν_5 and ν_{12} (at ~756 and 808 cm^{-1}) are measured at 759 and 791 cm^{-1} for C; both signals decrease in intensity in the beam of the spectrometer, with the appearance in the ν_{12} region of a new one at 801 cm^{-1}. Incidentally, the A_1 and B_1 CD_2 wagging modes, because of a strong coupling with the ring deformations, are expected to be much more shifted with respect to monomeric EO-d_4 upon complexation than the CH_2 corresponding modes which are not located in the same frequency range. This is the reason why we suggest assigning the band at 956.5 cm^{-1} instead of the one at 900 cm^{-1}, not sensitive to hydrogen bonding, to the ν_{11} (B_1) mode. The 900-cm^{-1} absorption is then assigned to the ν_{14} (B_2) mode which cannot be coupled to a ring mode even if the symmetry of the complex is lowered with respect to that of the isolated molecule (C_s instead if C_{2v}, as in the case of the EO:HF complex[8]).

In the presence of a large excess of EO with respect to HI and after annealing, two new broad bands are observed in the low-frequency region: the first one at 660 cm^{-1} (fwhm = 40 cm^{-1}) and the second around 1000 cm^{-1}, which displays ill-defined submaxima at 1055, 1045, and 970 cm^{-1} (Fig. 7 of ref 3). Both increase in intensity with the EO/HI molar ratio and are not sensitive to infrared irradiation. On the basis of the assignments proposed for the HI/dimethyl ether system,[9] these bands are assigned to the motion of the delocalized proton along the O··O axis in the 2:1 complex. According to this interpretation, this complex is considered as an ion pair, $(EO\cdot\cdot H\cdot\cdot EO)^+I^-$, in which the potential well along the O··O axis is either symmetrical or asymmetrical, depending on the symmetry of the surroundings, in particular on the position of the iodide counterion. In case of high symmetry there is perfect sharing of the proton, motion of which gives rise to the 660-cm^{-1} band; in the other case, the asymmetry is responsible for the frequency increase and for the band broadening. As for the corresponding bands of EO-h_4, it is difficult to assign them because of overlapping with those of the polymeric species. However, the presence of Evans holes at

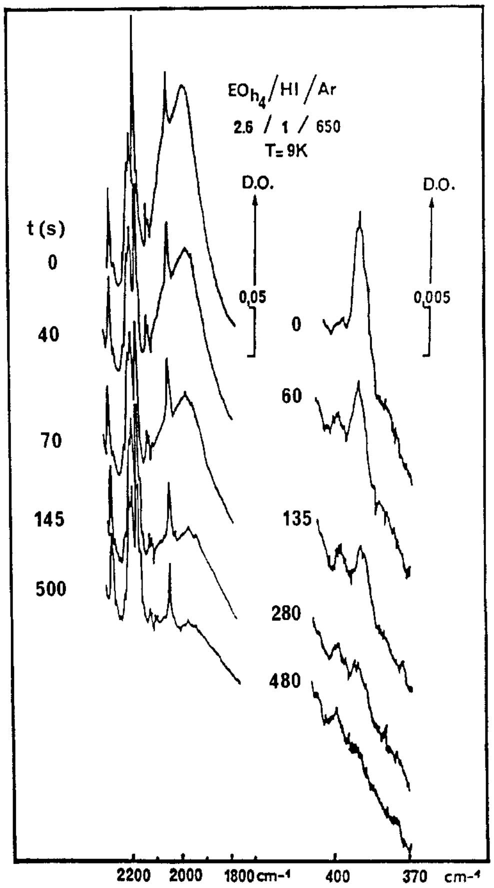

Figure 1. Irradiation effect on the ν_s and ν_l bands of the 1:1 EO-h_4:HI complex trapped in solid argon. Spectra recorded at T_s = 9 K for increasing times (seconds) spent by the sample in the light beam of the IR spectrometer.

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(8) Georgiou, A. S.; Legon, A. C.; Millen, D. J. *Proc. R. London*, **1981**, *A373*, 511.

(9) Loutellier, A.; Schriver, L.; Burneau, A.; Perchard, J.-P. *J. Mol. Struct.* **1982**, *82*, 165.

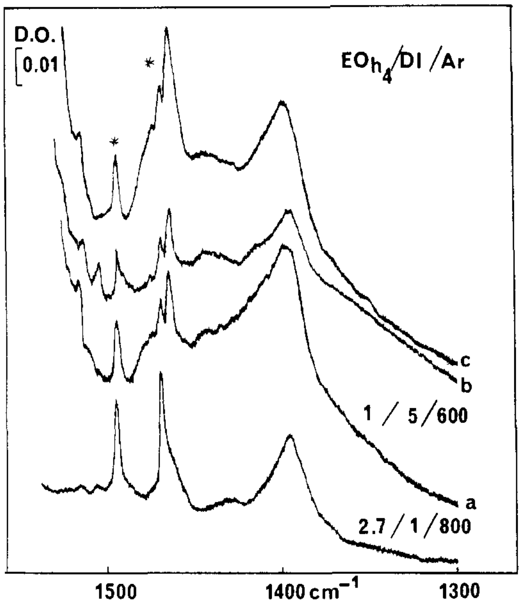

Figure 2. Temperature and irradiation dependence in the DI spectral region for EO-h_4/DI/Ar matrices: (a) after deposition, recording at T_s = 30 K; (b) after 100-min irradiation in the beam of the spectrometer at T_s = 9 K; (c) after annealing at 40 K for 10 min, recording at T_s = 30 K. Bands marked with an asterisk are of free EO-h_4.

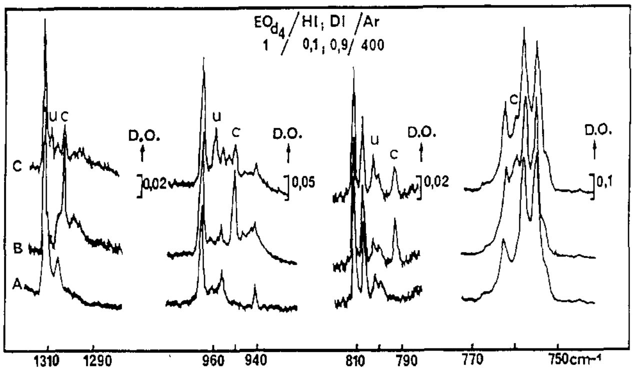

Figure 3. Temperature and irradiation dependence of the ν_2, ν_4 and ν_{11}, ν_{12}, ν_5 bands of EO-d_4 of the 1:1 EO-d_4:H(D)I complex trapped in solid argon: (A) spectrum of a EO-d_4/Ar binary mixture recorded at 30 K; (B) spectrum of a EO-d_4/H(D)I/Ar = 1/1/400 mixture recorded at 30 K just after deposition at 20 K in the dark; (C) spectrum of the same matrix recorded at Ts = 9 K after 110-min irradiation in the beam of the spectrometer at this temperature.

1476, 1133, and 835 cm^{-1} characterizes the frequencies of some of these modes (probably the symmetrical ν_2, ν_3, and ν_5 modes, respectively).

Experiments carried out at EO-h_4/HI molar ratios less than one lead to the observation of new features both in the HI and in the low-frequency regions. On the one hand, a broad band at 2020 cm^{-1} (fwhm = 130 cm^{-1}) overlaps the ν_s band of C after deposition but is well-identified after elimination of this second one by infrared irradiation. On the other hand, in the low-frequency region, the same kinds of features as those observed at EO/HI molar ratio greater than one are identified, namely, a band at 650 cm^{-1} (fwhm = 50 cm^{-1}) and a broad absorption between 700 and 1500 cm^{-1} with submaxima at 1365, 1230, 1105, 1055, 980, and 750 cm^{-1} and Evans holes at 1472, 1130, and 830 cm^{-1}. The low-frequency bands characterize large ionic aggregates involving probably both (IHI)$^-$ and (BHB)$^+$ species; as for the strong band at 2020 cm^{-1}, it could be assigned to HI molecules interacting with (IHI)$^-$.

3. EO/DI/Ar. Experiments carried out at EO-h_4/(D + H)I molar ratios varying between 3 and 0.2, and DI/(H + D)I isotopic ratios of 0.8–0.9, allow the observation of several product bands in the 1500–1350-cm^{-1} region. The strongest one is observed at 1397 cm^{-1} (fwhm = 25 cm^{-1}) (Figure 2); its intensity decreases upon infrared irradiation at 10 K in the beam of the spectrometer. Owing to the concentration effects, this band is assigned to the stretching modes ν_s of DI in the 1:1 complex C; the HI/DI isotopic ratio, 1.3958, is close to the values found for polymers of HI/DI trapped in argon.[10] Bands of EO engaged in the C complex are identified by their behavior on infrared irradiation; their frequencies are reported in Table III. The results obtained for DI/EO-d_4/Ar mixtures parallel those previously described, except for the ν_s band which is split into two components at 1411 and 1395 cm^{-1}. Since the two components are observed with the same relative intensity whatever the experimental conditions, we suggest that the splitting arises from a Fermi resonance between ν_s and either the first overtone of the CD$_2$ rocking (A$_2$) mode, 2ν_8, or the combination ν_{14} + ν_{15}, both expected at about 1400 cm^{-1}. Some frequencies of complexed EO-d_4 which have been clearly identified for both C and U species (Figure 3) are reported in Table III. Spectra obtained for samples with EO/DI molar ratios larger than one display weak additional features in the 1420–1520-cm^{-1} spectral range (Figure 2), but no band below 1000 cm^{-1}. These observations are different from thoose previously made for the EO/HI system and lead to the conclusion that the formation of n:1 aggregates does not gives rise to deuteron sharing. The same conclusion was reached in the dimethyl ether–hydriodic acid study,[9] in which the deuterium counterpart of the centrosymmetrical cation (BHB)$^+$ was not identified.

4. EO/HI/N$_2$. For dilute samples the hydrogen-bonded 1:1 complex was identified in the spectra recorded at about 25 K by a broad band at 1950 cm^{-1} (fwhm = 140 cm^{-1}) assignable to ν_s and by weak features due to complexed EO (Table III). All these bands disappeared when the sample was cooled to 9 K and exposed to the light beam of the spectrometer for 20 min. after irradiation of EO-d_4/HI/N$_2$ samples new bands blue-shifted by some wavenumbers with respect to those observed before irradiation and very close to EO-d_4 monomer bands were identified; they are unambiguously assigned to several modes of EO-d_4 belonging to the non-hydrogen-bonded form of the EO-d_4:HI complex whose ν_{HI} mode has not been identified, probably because of overlapping with the HI monomer band at 2237 cm^{-1}. At high concentration in both dopants the same low-frequency features as those described for Ar matrices were observed, namely, a relatively narrow band at 660 cm^{-1} (fwhm = 30 cm^{-1}) and a very broad absorption between 1500 and 800 cm^{-1} with submaxima and Evans holes. As discussed above, they characterize asymmetrical ionic species, in particular the (BHB)$^+$ cation responsible for the Evans holes due to Fermi resonance between the stretching mode of the proton and internal modes of the base. In the HI stretching region a new band at 1870 cm^{-1} is also evidenced, on the low-frequency side of the 1:1 ν_s band, which was not observed in Ar matrices.

For EO/HI molar ratios of the order of 0.35 two broad absorptions at 2020 and 1870 cm^{-1} frame the 1950-cm^{-1} one. They are better evidenced after irradiation which leads to the disappearance of the central one. The 1870-cm^{-1} band could be assigned to a HI molecule doubly perturbed on both ends by one EO and another HI molecule.

5. EO/DI/N$_2$. Substitution of HI by DI led to the observation of a broad band at 1390 cm^{-1} (fwhm = 45 cm^{-1}) with EO-h_4 or of a doublet at 1404–1388 with EO-d_4 assignable to ν_s of the deuterium-bonded form C of the 1:1 complex EO:DI. As in Ar matrices, the ν_s splitting of the EO-d_4:DI complex is explained by the existence of a Fermi resonance between ν_s and the first overtone of ν_8 or the combination ν_{14} + ν_{15}. Weak features assignable to complexed EO are also identified (Table III). Irradiation effects are scarcely observable and require long exposure time in the beam of the spectrometer to be detected.

The presence of an excess of EO-d_4 with respect to DI leads to broadening of the ν_s band with appearance of a noticeable shoulder at about 1425 cm^{-1}; no signal is detected below 1300 cm^{-1}. For the EO-d_4/DI ratio of the order of $^1/_3$ two relatively narrow lines are measured at 1455–1440 cm^{-1}; they are sensitive to the infrared beam of the spectrometer and decrease in intensity

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[10] Engdahl, A.; Nelander, B. *J. Phys. Chem.* **1986**, *90*, 6118.

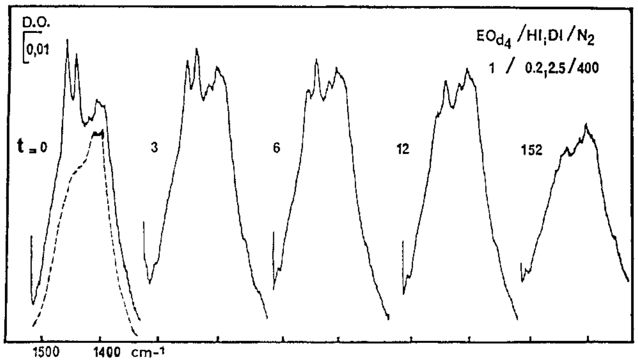

Figure 4. Irradiation effect on a EO-d_4/DI/N_2 = 1/2.7/400 matrix. Dotted line: spectrum recorded at T_s = 20 K after deposition at 20 K in the dark. Full line: spectra recorded at T_s = 9 K after 30 min in the dark at 30 K, for different times (minutes) of irradiation in the beam of the spectrometer.

faster than the ν_s band of the 1:1 complex upon irradiation at 9 K (Figure 4).

Interconversion Study of Two Forms of the 1:1 Complex

Framework of the C ⇄ U Interconversion Study. The kinetics of the photodissociation of the C form of the 1:1 complex has been studied either upon irradiation by the IR source of the spectrophotometer or in the dark. The corresponding data have been analyzed within the framework previously developed for the CH_3CN:HI complex trapped in argon.[2] The population evolution of C is governed by two competitive factors, namely, illumination $E(\nu)$ and temperature T_s of the sample. Vibrational excitation of C upon IR irradiation leads to C → U conversion while temperature increase allows the system to recover thermodynamic equilibrium through C ← U thermal conversion. Such a conversion depends on the height of the potential barrier stabilizing the metastable U form; if it is low enough, spontaneous tunneling can occur. Accordingly, three kinds of kinetic rate constants are introduced in the equation: $\vec{K}(\nu)$ for the photoprocess, $\overleftarrow{k}(T_s)$ for the thermal process, and $\overleftarrow{k}_{\text{tun}}$ for C ← U tunneling. The kinetic equation is then

$$dN_c/dt = -\vec{K}(\nu)N_c + [\overleftarrow{k}(T_s) + \overleftarrow{k}_{\text{tun}}](N - N_c) \qquad (1)$$

where N is the total number of 1:1 complexes in the sample and N_c the number of C species. Upon integration one gets

$$(N_c^{\infty} - N_c)/(N_c^{\infty} - N_c^{0}) = \exp(-kt) \qquad (2)$$

with

$$k = \vec{K}(\nu) + \overleftarrow{k}(T_s) + \overleftarrow{k}_{\text{tun}} \qquad (3)$$

the indexes ∞ and 0 referring to the steady state to the initial state, respectively. Kinetics data will be examined by using eq 2 and also taking into account the properties of the steady state characterized by the following relationship:

$$(N - N_c^{\infty})/N_c^{\infty} = \vec{K}(\nu)/[\overleftarrow{k}(T_s) + \overleftarrow{k}_{\text{tun}}] \qquad (4)$$

As shown below, varying the two parameters $E(\nu)$ and T_s allows to estimate the relative contributions of $\vec{K}(\nu)$, $\overleftarrow{k}(T_s)$, and $\overleftarrow{k}_{\text{tun}}$ to the C ⇄ U interconversion.

Photodissociation of C upon IR Irradiation. The C → U photoconversion of the EO:H(D)I complex trapped in argon or in nitrogen was studied at 10 K through the intensity decrease of the ν_{12} band at about 800 cm^{-1} for EO-h_4:HI and of the ν_s band around 1400 cm^{-1} for *EO-h_4*:DI. This choice was mainly guided by the value of the ratio between the time required for recording the band and the characteristic time τ of the photoprocess ($\tau = k^{-1}$). The small τ values (of the order of 100 s) for the EO:HI system requires short recording duration (less than 10 s); as a consequence, the narrow ν_{12} band recorded in 9 s was chosen, the possibility of examining the ν_s band spread over more than 200 cm^{-1} being excluded. In the case of EO:DI, the large τ value (of the order of 1000 s) made it possible to consider the ν_s band recorded in about 20 s. For EO:HI long irradiation time leads to complete disappearance of C. In other terms N_c^{∞} is null, which, according to eq 4, means that both $\overleftarrow{k}(10)$ and $\overleftarrow{k}_{\text{tun}}$ rate constants are negligible relative to $\vec{K}(\nu)$. Accordingly, eq 2 simplifies to

$$\ln N_c/N_c^{0} = -\vec{K}(\nu)t$$

TABLE IV: Values of the Kinetic Rate Constants (in 10^{-4} s^{-1}) for the Photodissociation of the C Form of the EO:HI Complex Trapped in Ar in the Light Beam of the Spectrometer at T_s = 9 K[a]

nature of the filter[a]	transmission at 1950 cm^{-1}, %	$\vec{K}'(\nu)$	$\vec{K}(\nu)$
no filter		96	96
neutral	75	70	93
	37	39	105
	25	24	96
IF1 (1700–2500 cm^{-1})	60	64	107
IF2 (500–900 cm^{-1})	0	6	
IF3 (2400–3400 cm^{-1})	0	10	

[a] $\vec{K}'(\nu)$ is the experimental value and $\vec{K}(\nu)$ the value corrected from absorption/reflection of the filters whose transmission at ν_s = 1950 cm^{-1} is given in the second column. For interference filters IF1, IF2, and IF3 the frequency domain with transmission greater than 0.4 is given in parentheses.

Plots of ln A/A_0, where A and A_0 are the peak absorbance or integrated intensity at time t and 0, respectively, versus time are seen to be linear, the slopes being reported in Table IV for different measurements. On the one hand, several kinds of neutral filters (ICs, Si) with constant transmission in the mid-IR were placed in front of the entrance window of the cryostat. The kinetic rate constants obtained with these filters are seen to vary proportionally to their transmission. This result is of course expected for a single-photon process and allows to check the accuracy of the measurements, probably not better than 10%. On the other hand, several interference filters were used, with their transmission domains reported in Table IV. For two of them, which have a null transmission between 900 and 2100 cm^{-1}, the kinetic rate constants are close to that of the dark process, leading to the conclusion that the efficient radiation domain for the C → U conversion lies in this interval. However, the $\vec{K}(\nu)$ value obtained with IF3 is believed to be significantly greater than the dark process one, which means that excitation of the CH stretching modes can induce the conversion. The most efficient filter, transmitting more than 40% in the range 1700–2500 cm^{-1}, gives rise to a $\vec{K}(\nu)$ value comparable to that in the absence of a filter, after absorption correction. Thus, the main efficient modes for the C → U conversion are ν_s of HI and the two CH_2 bending modes of EO at about 1470 cm^{-1}. (At this frequency the transmission of the filter is 0.2.)

The C → U conversion of the EO-h_4:DI complex was examined only in the absence of a filter, because of the very slow conversion rate. The $\vec{K}(\nu)$ value is found to be of the order of 1.7 × 10^{-4} s^{-1}, which means that probably only the CH stretching modes of complexed EO contribute to the conversion. In other words, the C → U barrier height is greater than 1400 cm^{-1} so that the vibrational excitation efficient for the C → U conversion in the EO-h_4:HI pair is probably ν_s. Some experiments were also carried out in nitrogen matrices, in the absence of a filter. The results, gathered in Table V, evidence a decrease of the $\vec{K}(\nu)$ value by a factor of 2 from Ar to N_2, larger than observed for the CH_3CN:HI complex (Table V).

Study of the Dark Process. Two experimental procedures were used in the kinetic study of the dark process. In the first one, the temperature of the sample was kept at 31 (Ar) or 29 K (N_2) for 15 min in the dark and then quickly adjusted at T_s. As shown below, the C → U conversion can be considered as totally achieved at about 30 K in the dark so that $N_c^{0} = N$ at time t = 0. In the second procedure, the sample was firstly maintained at 9 K for 15 min in the beam of the spectrometer source, which leads to the complete disappearance of C. Then the temperature of the sample was quickly adjusted at T_s. Thus, N_c^{0} = 0 at time t = 0. The kinetics of the C → U interconversion was measured

TABLE V: Comparison between Properties of the C $\rightleftarrows$ U Interconversion of the EO:H(D)I and CH_3CN:H(D)I Complexes Trapped in Ar and N_2 Matrices[a]

		Ar		N_2	
		HI	DI	HI	DI
EO:H(D)I	$\vec{K}(\nu)$	96	1.7	42	1
	$\vec{K}_{DP}$	6	0	4	0
	E_a	3.4	5.5		
CH_3CN:H(DI)	$\vec{K}(\nu)$	70	31	57	11
	$\vec{K}_{DP}$	2[b]	2.5	1.2	1.7
	E_a	1.5	2.1		

[a] Kinetic rate constants in 10^{-4} s^{-1}, $E_{C \leftarrow U}$ in J/mol. [b] After subtraction of the tunneling rate constant.

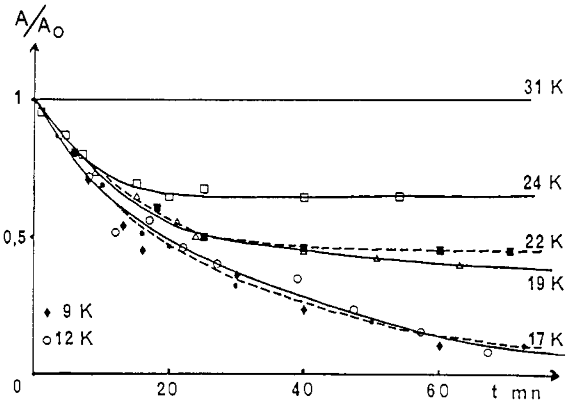

Figure 5. Time development of the normalized optical density (A) of ν_{12} at 801.5 cm^{-1} of EO-h_4 belonging to the C form of the EO-h_4:HI complex trapped in argon for different temperatures in the dark. Each spectrum was recorded in 9 s through interference filter IF2 transmitting between 500 and 900 cm^{-1}.

through the intensity decrease (method 1) or increase (method 2) of one band of C recorded by using the appropriate interference filter which minimizes irradiation from the IR spectrometer source during recording. The necessity of using these two different procedures stems from results displayed in Figure 5. For values of T_s less than 18 K, C totally disappears in the dark, which allows method 1 to be used for determining the kinetic rate constants with a good accuracy. For T_s values above 18 K, C decreases only partially, the less so as temperature increases, so that method 2 is more appropriate for the determination of the rate constant. The various measurements lead to two main conclusions, the first one confirming the role of the thermal bath on the C photodissociation and the second quantifying the role of T_s on the thermal C ← U conversion.

(*a*) *Role of the Radiation Shield.* As described in paper 2, the sample holder screwed on the lower part of the liquid helium Dewar is surrounded by a radiation shield maintained at 80 K. This radiation shield is drilled with four holes: two for the gas inlets and two for the spectroscopic observations, along the optical axis of the cryostat (Fig. 1 of paper 2). Two series of experiments were performed at $T_s = 9$ K in argon using two different radiations shields, with optical aperture of 0.3 and 0.13 sr corresponding to hole diameters of 25 and 10 mm, respectively. Kinetic studies performed at $T_s = 9$ K for an EO-h_4/HI/Ar mixture lead to the kinetic rate constant values of 6×10^{-4} and 3×10^{-4} s^{-1}, respectively, nearly in the same ratio as that of the irradiation solid angles ($6/3 = 2.0$ against $0.3/0.13 = 2.4$). This result is another proof of the role of radiation thermal bath on the C → U conversion.

(*b*) *Comparison between $\vec{K}_{DP}$ and $\vec{K}(\nu)$.* In the hypothesis where the C → U conversion is mainly monitored by the vibrational excitation of the ν_s mode, the kinetic rate constants measured at 9 K are expected to be proportional to the illumination of the sample at ν_s frequency, namely, 1950 cm^{-1} (EO:HI) or 1400 cm^{-1} (EO–DI); one can then write

$$\vec{K}(\nu)/\vec{K}_{DP} = E(\nu_s)/E_{DP}(\nu_s)$$

TABLE VI: Temperature Dependence of the C $\rightleftarrows$ U Interconversion As Measured in the Dark for EO-h_4:HI Trapped in Ar[a]

			$\overleftarrow{k}(T_s)$	
T_s, K	N_c/N	k	eq 5	eq 6
17	0	6	0	0
19	0.33	9.2	3.2	3.1
22	0.47	12.5	6.5	5.9
23	0.53	13.8	7.8	7.3
24	0.64	26.5	20.5	17.0
25	0.78	38.9	32.9	30.3
26	0.92	134	128	123
28	0.98	222	216	218

[a] Determination of the values of $\overleftarrow{k}(T_s)$ according to eq 5 and 6. Kinetic rate constants in 10^{-4} s^{-1}.

The values of E obtained in paper 2 for irradiation by the source of the spectrometer and by the thermal bath have been recalled in the experimental part of this paper (eq 1 and 2). The emittance β of the source of the spectrometer is taken equal to 0.86 and 0.90 at $\nu = 1950$ and 1400 cm^{-1}, respectively. Then the illumination from the source in the frequency interval (ν_s, $\nu_s + \Delta\nu$) is (in 10^{-12} W/m) $E_S(\nu_s) = 2.9\Delta\nu$ and $2.2\Delta\nu$ at $\nu_s = 1950$ and 1400 cm^{-1}, respectively. The illumination from the thermal bath at 295 K is (in the same units) $E_{DP}(\nu_s) = 0.14\Delta\nu$ and $0.73\Delta\nu$ at $\nu_s = 1950$ and 1400 cm^{-1}, respectively. Consequently, the ratio of the kinetic rate constants are expected to be $\vec{K}(\nu)/\vec{K}_{DP} = 2.9/0.14 = 21$ for the EO:HI pair and $\vec{K}(\nu)/\vec{K}_{DP} = 2.2/0.73 = 3$ for the EO:DI pair. Experimentally, the ratios have been measured for the EO:HI complex trapped in argon and nitrogen and found equal to 16 (Ar) and 11 (N_2) (Table V). The order of magnitude appears to be satisfactory, but the agreement is far from being quantitative, especially in the case of the nitrogen matrix. This discrepancy, however, is not surprising, taking into account the difficulty of obtaining an accurate determination of the sample illumination. As for the EO:DI system, the measurements are not accurate because of excessively slow C → U conversion. The $\vec{K}_{DP}$ value has been taken equal to zero, because no intensity decrease of the bands of C was detected after 1 h in the dark at 9 K. If $\vec{K}_{DP}$ is really null, this result means that the hypothesis of the efficiency of ν_s is not realistic since in this case $\vec{K}_{DP}$ should reach a value of about 5×10^{-5} s^{-1} in argon (corresponding to an intensity decrease of 17% for C after 1 h in the dark). Then, the nonnull value of $\vec{K}(\nu)$ would originate from high-frequency IR radiations (say, 3000 cm^{-1}) which are not significantly emitted by the laboratory thermal bath.

(*c*) *Temperature Dependence of the Kinetic Rate Constant.* The time development of ln $(A^\infty - A)/(A^\infty - A^0)$ obtained for EO:HI in argon with experimental procedures 1 and 2 according to T_s is linear. The values of the kinetic rate constant k deduced from the slopes are seen to be temperature independent below 17 K and then to increase very fast with T_s above 17 K. Use of relationships 3 and 4 allows $\overleftarrow{k}(T_s)$ to be determined according to two different methods. Use of eq 3 and taking into account that $\overleftarrow{k}(T_s)$ is negligible below 17 K and furthermore that there is no C ← U tunneling lead to

$$\overleftarrow{k}(T_s) = k - \vec{K}_{DP} \tag{5}$$

$\vec{K}_{DP}$ being identified with k below 17 K. On the other hand, relationship 4 can be written as

$$\overleftarrow{k}(T_s) = kN_c^{\infty}/N \tag{6}$$

in which N is identified as N_c^0 in an experiment where the sample is kept at 30 K in the dark for at least 15 min. Values of $\overleftarrow{k}(T_s)$ obtained in both case are displayed in Table VI. The agreement is good and strongly confirms the overall interpretation of the C $\rightleftarrows$ U interconversion. In the hypothesis of an Arrhenius behavior for $\overleftarrow{k}(T_s)$ above 20 K

$$\overleftarrow{k}(T_s) = A \exp(-E_{C \leftarrow U}/RT_s) \tag{7}$$

one gets an activation energy $E_{C \leftarrow U}$ for the C ← U conversion of 3.4 kJ/mol from the plot of ln $\overleftarrow{k}(T_s)$ versus $1/T_s$. The same

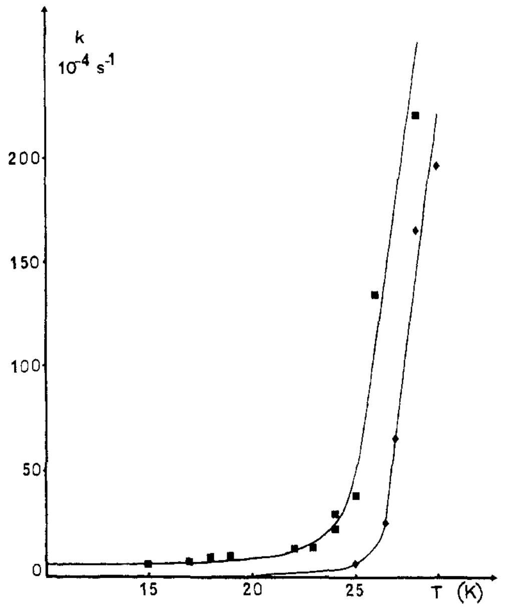

Figure 6. Temperature development of *k*. Measurements were performed in the dark, the irradiation occurring from the laboratory thermal bath (295 K). ■, EO/HI/Ar; ◆, EO/DI/Ar.

experiments were carried for EO/DI/Ar mixtures. The values of *k* according to T_s are displayed in Figure 6. Since $\bar{K}_{DP}$ is null, $\bar{k}(T_s)$ is simply identified as *k*; use of eq 7 above 22 K allows one to get an activation energy $E_{C\leftarrow U}$ of 5.5 kJ/mol.

Conclusion

In this paper we have examined the spectral properties of matrix-isolated hydrogen-bonded complexes between one of the strongest acids, hydrogen iodide, and ethylene oxide (proton affinity 183 kcal/mol). The 1:1 complex is typical of medium-strength hydrogen bonding, with a relative HI frequency shift with respect to monomer of 0.125. This complex (C), as several others involving weak bases such as CH_3CN and H_2O interacting with HI, is sensitive to infrared irradiation and photodissociates into another non-hydrogen-bonded form (U) whose several vibrations have been identified. The interconversion processes between C and U have been examined. The conclusions are the same as those previously drawn for the CH_3CN:HI pair, with minor differences tied to a change in barrier height between the C and U forms. This barrier is higher for EO:HI than for CH_3CN:HI, and the most remarkable consequence is the weak photosensitivity of the EO:DI C species, the excitation of its ν_s mode at 1400 cm^{-1} being unable to overcome the barrier for the C → U conversion. This conversion should then proceed through excitation of the CH stretching modes and, possibly, the first overtone of ν_s. Similarly, the barrier height for the C ← U conversion, as deduced from the temperature dependence of the kinetic rate constant, is 3 times greater for EO:HI so that no tunneling is observed for this system. Larger $(EO)_m(HI)_n$ aggregates were also identified by low-frequency broad bands typical of proton transfer, with formation of ionic species such as $[(EO)_2H]^+$ and possibly $(IHI)^-$. Unfortunately, we were not able to determine the precise stoichiometries of these complexes, probably because any aggregate with $m \geqslant 2$ gives rise to the same ionic species. Deuterium counterparts of these ions were not detected, which means that the breaking of the D–I bond does not occur. Instead, new bands were observed in the DI spectral region, some of them being photosensitive.

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Registry No. EO, 75-21-8; HI, 10034-85-2; DI, 14104-45-1; C_2D_4, 683-73-8; EO-d_4, 6552-57-4; 1,2-dibromoethane-d_4, 22581-63-1; 2-chloroethanol-d_4, 117067-62-6.

Shared Electronic Excitations in Clusters of Cyclopentanone. Mixed Isotope Studies Using Optically Detected Magnetic Resonance

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We report zero-field optically detected magnetic resonance (ODMR) studies of neat, polycrystalline samples of cyclopentanone-d_0, cyclopentanone-d_4, cyclopentanone-d_8, and mixtures of these compounds cooled to 1.4 K and excited with a broad-band mercury arc. The ODMR spectra of the pure deuteriated compounds each exhibit nine lines, of different signs and unusually narrow widths, as in the case of the protonated compound [Shain, A. L.; Sharnoff, M. *Chem. Phys. Lett.* **1973**, *22*, 56]. Concentration-dependent shifts in the frequencies, widths, and relative intensities of these lines are observed in the isotopically mixed samples. The results may be satisfactorily interpreted by assuming that the spectrum is that of a cluster in which the triplet excitation is shared by three or more translationally inequivalent molecules having well-defined orientations with respect to each other.

Introduction

Photoexcited cyclopentanone and its derivatives have been the subject of several studies using the optically detected magnetic resonance (ODMR) technique, especially by Sharnoff and coworkers.[1-5] Among the results obtained, perhaps the most interesting was the finding[4] that pure, polycrystalline samples cooled to 1.4 K exhibit a zero-field (zf) ODMR spectrum consisting of nine lines rather than the three lines expected for an isolated molecule in its lowest triplet state. The nine lines, which are both positive and negative in sign, can be grouped into three triads, suggesting the simultaneous existence of three different triplet states. The observed ODMR line widths are also unusually small, 5–10 MHz, which is surprising for a polycrystalline sample. Similar results were obtained for cyclopentanone dissolved at low

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