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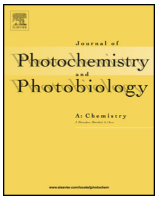

Full length article

New aspects of UV photolysis of hydrogen peroxide. Nitrogen matrix isolation FTIR and theoretical studies

Justyna Krupa, Maria Wierzejewska*

Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383, Wrocław, Poland

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ABSTRACT

UV photochemistry of H_2O_2 isolated in solid nitrogen at 15 K has been studied experimentally by FTIR matrix isolation technique and theoretically using DFT and MP2 methods. The major photoproducts were identified as (i) nitrous oxide and $N_2O\cdots H_2O$ complex and (ii) free and complexed to N_2O hydroxyl radicals. Except for the OH radicals all observed species are unique and characteristic for H_2O_2 photolysis in solid nitrogen. The identities of the products have been confirmed by comparison with results of quantum chemical calculations, and reference to the spectral data of related molecules. Differences in the photolysis course upon irradiation at 230 and 212 nm are discussed.

1. Introduction

H_2O_2 is an important atmospheric species playing a significant role in the gas phase oxidation reactions and combustion processes in Earth's atmosphere. It has an important impact in the production and fate of hydroxyl and peroxyhydroxyl radicals in the troposphere [1,2]. Due to a high solubility of H_2O_2 in water it matters in reactions proceeding in aqueous solutions and in water droplets. Since its detection in the cloud core ρ Oph A, hydrogen peroxide is also expected to be a key species in the water and oxygen chemistry in the interstellar medium [3]. It was found that the H_2O_2 molecule on the dust grains is an important intermediate in the formation of water [4]. Hydrogen peroxide formation was observed in situ by laboratory infrared spectroscopy in the ion irradiated H_2O-ice at temperature relevant to extraterrestrial surfaces (20–120 K) [5] that explained the detection of H_2O_2 on Europa [6].

Weakly bound molecular complexes play an important role in the chemistry of Earth's atmosphere [7–11]. Such species have recently been considered as potential contributors to chemistry of interstellar media and planetary atmospheres [7,10]. Among them are complexes of water or OH radical with different atmospheric species. Some of them are a subject of this paper.

Infrared spectra of hydrogen peroxide are well-known in the gas phase [12–14].

A number of papers have also been published on hydrogen peroxide isolated in low temperature matrices of noble gases and its UV photolysis [15–20]. From among several photodissociation channels available for hydrogen peroxide in the gas phase only two take place after UV photolysis at 193 nm or 248 in argon matrices [19,20]. Two main products, namely the OH radicals and the $H_2O\cdots O(^3P)$ complex, were identified in solid argon on the basis of the isotopic substitution and ab initio calculations [20]. In turn, in solid krypton and xenon the $H_2O\cdots O$ complex was formed with less efficiency indicating other photolysis channels existed in these cases. The HOO radical (free or complexed) was assigned as an additional product in Kr and Xe matrices. In the light of the above differences we found interesting to perform H_2O_2 photolysis in relatively strongly interacting, as compared with rare gas solids, nitrogen matrices. Herein we combine experimental FTIR matrix isolation technique and theoretical calculations to get reliable data of the photolysis processes proceeding in solid nitrogen and to compare them with the existing data on H_2O_2 phototransformations in rare gas matrices.

2. Experimental and computational details

2.1. Matrix isolation FTIR studies

Hydrogen peroxide was obtained from urea hydrogen peroxide adduct (UHP, Aldrich, 98%) in a similar way as described by Pettersson et al. [17]. A small amount of the adduct was placed in a glass bulb held at 0–5 °C situated outside the cryostat chamber. The gaseous H_2O_2 released during the UHP decomposition was mixed with a large excess of nitrogen (Messer, 6.0) and such mixture was

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* Corresponding author.
E-mail address: maria.wierzejewska@chem.uni.wroc.pl (M. Wierzejewska).

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deposited onto a CsI window kept at 15 K. The H_2O_2/N_2 matrices for the photolysis experiments have been prepared in such a way that hydrogen peroxide was mostly present in monomeric form. Low temperature was obtained by means of a closed cycle helium refrigerator (Air Products ARS-2HW) and measured by a silicon diode sensor working with a digital controller (Scientific Instruments, model 9700). Infrared spectra (4000–400 cm^{-1}) were collected in the transmission mode, with 0.5 cm^{-1} resolution, using a Bruker IFS 66 spectrometer equipped with a MCT detector.

The H_2O_2/N_2 samples were irradiated with the UV light provided by the frequency doubled signal beam of a pulsed (7 ns, repetition rate of 10 Hz) optical parametric oscillator Vibrant (Opotek Inc.), pumped with a Nd:YAG laser (Quantel).

2.2. Computational methods

All calculations were performed with the Gaussian 09 program package [21] using Density Functional Theory with the B3LYP [22–24], B3LYPD3 [25,26], B2PLYPD3 [27] functionals and ab initio second-order Møller-Plesset perturbation theory MP2 [28–32] methods. A large 6–311++G(3df,3pd) basis set was applied. For complexes formed between photoproducts the interaction energies have been obtained by subtracting the energies of the isolated monomers with the frozen geometry from the energy of the complexes. Both basis set superposition error by the Boys-Bernardi full counterpoise method [33] and zero-point vibrational energy corrections were included. Vibrational wavenumbers and intensities were calculated for the optimized structures at the same levels of theory.

3. Results and discussion

3.1. H_2O_2 monomer spectrum in nitrogen matrix

Fig. 1 compares the key regions of the infrared spectra obtained for H_2O_2/N_2 and H_2O_2/Ar matrices. The latter spectrum agrees well with that published earlier [17]. As shown in Table 1, for solid nitrogen the positions of the H_2O_2 monomer bands are, as expected, slightly red (OH stretches) or blue (OH bending) shifted in comparison with the corresponding absorptions reported for the H_2O_2/Ar matrices. In addition, the remarkable intensity changes of the H_2O_2 bands are observed when going from solid argon to nitrogen. The approximate values of the integrated intensity ratio for $\nu_1(\nu_5)$ and ν_6 bands are equal to 0.30 and 1.40 for argon and nitrogen experiment, respectively. Thus, a strong increase of the OH stretching modes (ν_1, ν_5) is observed due to interaction of the solute with the N_2 surrounding.

Table 1
Comparison of calculated (gas phase) anharmonic wavenumbers of the H_2O_2 monomer with the experimental infrared band positions in argon and nitrogen matrices.

B3LYPD3 6-311++G(3df,3pd)		Experimental		Assignment
		H_2O_2/Ar [a]	H_2O_2/N_2	
ν_{anh} (cm^{-1})	I (km mol^{-1})	ν (cm^{-1})	ν (cm^{-1})	
3583	9	3597	3585.5	ν_1
3585	46	3587.8	3580.5	ν_5
2657	5	2653	2676	$\nu_2+\nu_6$
		2643.6		$\nu_2+\nu_6$
1398	1	n.o. [b]	n.o.	ν_2
1275	100	1277	1294	ν_6
		1270.9		ν_6
927	1	n.o.	n.o.	ν_3

[a] Reference [17].
[b] Not observed.

The worth noting is also disappearance of the doublet structure of the ν_6 absorption in the H_2O_2/N_2 spectrum. Such splitting observed in the spectra of noble gas matrices was attributed [17] to the tunneling effect that results from the double minimum appearing due to internal rotation in H_2O_2 [34,35]. Apparently, in strongly interacting nitrogen matrices the extent of the splitting is modified and lowered comparing with the argon environment.

3.2. Photochemistry of H_2O_2 in solid nitrogen

3.2.1. Main photolysis pathways

In addition to the photolysis studies performed in nitrogen matrices, the analogous experiments were conducted also for H_2O_2 in solid argon. The latter were in good agreement with those reported in the literature [20]. When H_2O_2/N_2 matrices were

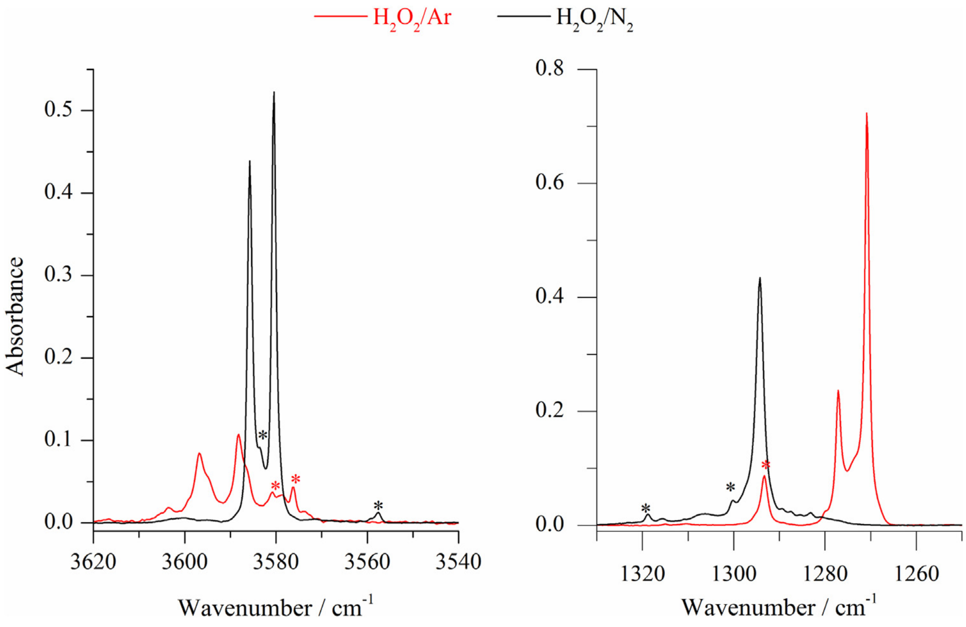

Fig. 1. OH stretching and bending regions of H_2O_2)isolated in N_2 matrix (black trace) and Ar matrix (red trace). Dimer/multimer absorptions are marked with asterisk (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.