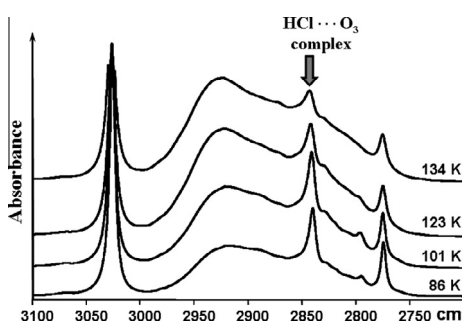


IR spectroscopic study of the HCl···O<sub>3</sub> molecular complex in liquid argonK.M. Bulanin<sup>a,\*</sup>, V.P. Bulychev<sup>a</sup>, W. Herrebout<sup>b</sup>, D.N. Schepkin<sup>a</sup><sup>a</sup> Department of Physics, St.- Petersburg State University, Peterhof, St. Petersburg 198504, Russia<sup>b</sup> Department of Chemistry, University of Antwerp, Antwerpen, Groenenborgerlaan, 171, B 2020 Antwerpen, Belgium

## HIGHLIGHTS

- We have detected the HCl···O<sub>3</sub> van der-Waals complex in liquid Ar solution by FTIR spectroscopy for the first time.
- Temperature dependence was investigated; the enthalpy of complex formation was determined to be  $\Delta H^\circ = 4.74 \pm 0.30 \text{ kJ mol}^{-1}$ .
- Structure, geometrical parameters and the binding energy ( $6.3 \text{ kJ mole}^{-1}$ ) of the complex were calculated.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 16 May 2013

Accepted 30 August 2013

Available online 7 September 2013

## Keywords:

Ozone  
Hydrogen chloride  
Cryospectroscopy  
FT-IR spectroscopy  
Molecular complexes

## ABSTRACT

Infrared spectra are reported of ozone and HCl dissolved in liquid argon (86–134 K) at concentrations varying from  $5 \times 10^{-5}$  to  $9 \times 10^{-6}$  M for HCl, and from  $1 \times 10^{-3}$  to  $5 \times 10^{-5}$  M for ozone. At low concentrations of O<sub>3</sub> and of HCl, no spectral features due to O<sub>3</sub>–HCl complex were found. At higher concentrations ( $1 \times 10^{-3}$  of ozone vs  $5 \times 10^{-5}$ – $9 \times 10^{-6}$  of HCl), a new band near  $2840 \text{ cm}^{-1}$  due to the HCl···O<sub>3</sub> complex was observed. FWHM of  $\nu_{\text{HCl}}$  of the complex is  $8 \text{ cm}^{-1}$ . From the temperature dependence of the absorption band intensity, the enthalpy of the complex formation was estimated,  $\Delta H^\circ = 4.7 \pm 0.4 \text{ kJ mole}^{-1}$ . The optimized geometry of the *cis*-HCl···O<sub>3</sub> complex and a value of  $6.3 \text{ kJ mole}^{-1}$  for its binding energy were determined by ab initio calculations.

Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.

## Introduction

Weak molecular complexes are of significant interest for the perturbing effect of one molecule on the other and for their structure. Detailed studies of monomer spectra of O<sub>3</sub> in liquid Ar and HCl in the same cryosolvent were reported previously [1,2]. The rotational fine structure of HCl is visible at lower temperature reached at our experimental conditions and becomes more pronounced at higher temperature. It was suggested that this is the effect of the solvent density variation with the temperature [2].

The broad range of molecular complexes involving ozone has been spectroscopically investigated by now (see for example, [3,4

and references therein]). However, as was mentioned before [5], weakly bound complexes of ozone with hydrogen halides, especially HCl, are scarcely studied, in spite of the fact that these complexes are of particular interest in the atmosphere.

Ozone as well as HCl molecules and their complexes were studied using widespread matrix isolation technique. However, this method does not allow quantitative measurements in a relatively broad temperature range, while the molecular cryospectroscopy method is devoid of these shortcomings [6].

The far-infrared spectra of the gas phase complexes in the HCl – noble gas mixtures were investigated by Boom and van der Elsken [7]. One type of intensively studied systems are the base – hydrogen halide van der Waals complexes [5,9]. Oligomeric species of hydrogen chloride as well as its complexes with different molecules were under considerable interest for a long time [2,8].

\* Corresponding author. Tel.: +7 (812) 4284462.

E-mail address: [kbulanin@mail.ru](mailto:kbulanin@mail.ru) (K.M. Bulanin).

Herrebut et al. [8] have investigated the ethene–HCl complex in cryosolutions in liquid argon and liquid nitrogen. Spectroscopic evidence for existence of the 1:1 and 1:2 complexes was found. Using spectra recorded at different temperatures, the complexation enthalpy  $\Delta H^\circ$  for both 1:1 and 1:2 systems was determined.

Molecular complexes of  $O_3$  with different molecules were also studied experimentally in different cryomatrixes [9–16]. Quantum chemical calculations of such systems have been done also [5,15]. The review on the ozone – base complexes in different cryomatrixes can be found in [3].

Spectra of the  $O_3$ –HF complex trapped in argon matrix including isotopic ozone modifications were studied by Andrews and co-workers [9]. All three perturbed ozone fundamentals were detected for this complex. It was found that ozone is attached to HF via its terminal oxygen atom. Tachikawa performed ab initio MO calculations for the same system in order to elucidate the structures and energetics of the complex [5]. It was found that the hydrogen atom of HF orients toward one of the oxygen terminal atoms. The calculations predicted the existence of *cis*- and *trans*-isomers.

Chemical reactions involving ozone in cryomatrixes have been under investigation as well. Ault [17] has performed the matrix isolation spectroscopic investigation of different alkenes with ozone.

Medcraft [18] has experimentally studied the  $O_3$ –HCl aerosols by means of FTIR spectroscopy. These systems were generated from mixtures of ozone and HCl at low temperatures. However, even at 80 K no experimental evidence of the existence of the  $O_3$ –HCl complex was found.

In addition, ozone was previously studied in adsorbed state at the liquid nitrogen temperature. It was found that it could form stable complexes with the superficial Lewis acid sites of some metal oxides, acting as a weak base [19]. Interacting with the Bronsted acid sites (superficial OH-groups), ozone forms hydrogen bond via its terminal oxygen atom [20].

To the best of our knowledge, no experimental results on molecular complexes involving  $O_3$ , and in particular HCl– $O_3$  complex, in cryosolutions and in the gas phase were published yet. Here we report for the first time the experimental spectroscopic data of the (1:1) molecular complex of ozone with hydrogen chloride in liquid argon solution. Ab initio MO calculations were carried out in order to determine the optimized geometry of the complex.

## Experimental part

The spectra were recorded using a Bruker IFS-66 FT-IR spectrometer, equipped with liquid nitrogen-cooled MCT detector at  $0.5\text{ cm}^{-1}$  resolution, by averaging 1000 scans and applying Happ–Genzel apodization. Fourier transformed data with the zero-filling factor of 4 were further treated using OPUS 6.0 and Fityk 0.9.4 software. The low temperature sample cell of 70 mm-long optical path, equipped with ZnSe internal windows and KBr external windows and cooled by liquid nitrogen, was designed to safely withstand internal pressures up to 25 bar for temperature variation. Spectral measurements were made in the 86–134 K temperature range, controlled by a pair of PT100 thermoresistor sensors. Solutions were prepared by introducing first measured amounts of the  $O_3$  and HCl gases to the sample cell pre-cooled to 86 K, and then filling it with a pressurized and rapidly liquefying argon gas. This procedure proved to result in a full dissolution of the solute species previously condensed on the internal cold cell walls. Solute concentrations (mole fractions) studied covered ranges of  $5 \times 10^{-5}$ – $9 \times 10^{-6}$  for HCl and  $1 \times 10^{-3}$ – $5 \times 10^{-5}$  for ozone.

Ozone samples were prepared from gaseous oxygen supplied by l'Air Liquid of 99.95% purity using Purusaqua O3-3000B ozone

generator. Argon used as a solvent was obtained from Alphagas and had stated purity of 99.9999%. Hydrogen chloride was of 99% purity (Sigma Aldrich).

## Computational details

The calculation of the optimized geometry of the 1:1 complex in *cis*-configuration was performed by the QCISD/6-311++G(2d,2p) method with the basis set superposition error taken into account using the GAUSSIAN 03 package [21].

## Results and discussion

### 4.1 Spectra of the HCl ··· $O_3$ complex

Spectra of pure ozone and pure HCl dissolved in liquid Ar at 86 K are shown in Fig. 1 (curves 1 and 2, respectively). The absorption bands of ozone at  $2774.7\text{ cm}^{-1}$  and  $3026.0\text{ cm}^{-1}$  correspond to the  $\nu_1 + \nu_2 + \nu_3$  ( $B_1$ ) and  $3\nu_3$  ( $B_1$ )  $O_3$  vibrations, respectively (Fig. 1, curve 1) [1]. A broad feature with the maximum near  $2921.0\text{ cm}^{-1}$ , present in the spectrum at higher HCl concentration (Fig. 1, curve 2), corresponds to the fundamental mode  $\nu_{\text{HCl}}$  of the monomeric hydrogen chloride. Additional weak features at  $2854.0$  and  $2828.0$ ,  $2797.0$ , and  $2762.0\text{ cm}^{-1}$  were previously attributed to the dimeric, trimeric, and tetrameric hydrogen chloride species, respectively [2]. Moreover, at the lowest temperatures reached in our experiments with higher HCl concentrations, two additional broad bands were seen at  $2755.0$  and  $2702.0\text{ cm}^{-1}$  (not shown), which can be attributed to polycrystalline hydrogen chloride [6,22,23].

In order to determine suitable conditions for minimization of the amount of oligomeric HCl species and maximization of the complex yield, the series of experiments were performed with different concentrations of ozone and hydrogen chloride. In the case of low ozone concentration ( $5 \times 10^{-5}\text{ M}$ ) and the HCl: $O_3$  ratios from 1:1 to 1:10, there were no any new features observed in IR spectra of HCl +  $O_3$  solutions in liquid argon at 86 K. Therefore, we can conclude that HCl ···  $O_3$  complex is not formed at these conditions, most probably because not enough ozone is present in solution to induce the formation of the measurable amount of the complex.

In the case of significant excess of ozone ( $1 \times 10^{-3}\text{ M}$ ) in HCl +  $O_3$  solution (the HCl concentrations were  $9 \times 10^{-6}\text{ M}$  and  $5 \times 10^{-5}\text{ M}$ ), the spectra at 86 K show the appearance of the distinct new feature at  $2840.3\text{ cm}^{-1}$  (Fig. 1, curves 3 and 4). This new band was not present when either reagent was separately added into liquid argon (curves 1 and 2). Augmentation of the

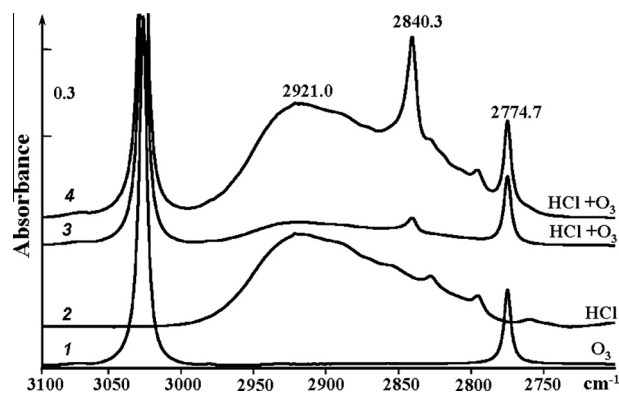


Fig. 1. IR spectra of: 1, 2 – pure ozone and pure HCl dissolved in liquid Ar, respectively; 3, 4 – ozone and HCl mixture in liquid argon solution at the HCl concentrations of  $9 \times 10^{-6}\text{ M}$  and  $5 \times 10^{-5}\text{ M}$ , respectively. All spectra were recorded at significant excess of ozone ( $M=1 \times 10^{-3}$ ) at 86 K.

Download English Version:

<https://daneshyari.com/en/article/7673235>

Download Persian Version:

<https://daneshyari.com/article/7673235>

[Daneshyari.com](https://daneshyari.com)