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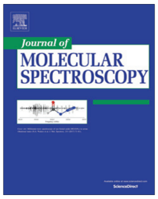

Infrared and density functional theory studies of isoprene-water complexes in noble gas matrices

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ABSTRACT

The interaction of 2-methyl-1,3-butadiene (isoprene) with a H_2O molecule in low-temperature noble gas matrices (Ar or Kr) was investigated using infrared absorption spectroscopy. Vibrational peaks arising from 1:1 isoprene-H_2O adducts were assigned and compared with the results of quantum chemical calculations. The comparison led to the conclusion that the H_2O molecule in the complex preferentially H-bonds to one of the two unsaturated C=C bonds, and that the binding energy of the complex is comparable to that of the C_6H_6-H_2O complex. The present study suggests that the change in the charge distribution of isoprene due to the formation of a complex with H_2O may lead to alteration of the reactivity with respect to the insertion of OH radicals, thereby influencing the formation of aerosols in the atmosphere.

1. Introduction

Isoprene is one of the most abundant volatile organic compounds (VOCs) in the troposphere with a global emission of ~500 Tg per year [1]. It reacts with OH radicals, ozone, and NO_x to produce low-volatility compounds, which are finally converted to secondary organic aerosols (SOAs) via subsequent complex physico-chemical processes, influencing the climate and urban air quality [2]. In this respect, the reaction of isoprene and OH radicals—the first step to SOA formation—has attracted much attention, and has been extensively studied both experimentally [3–6] and theoretically [3,4,7–11].

It has been shown that water molecules play an important role in environmental and atmospheric chemistry by forming hydrogen bonds (H-bonds) with other molecules [12]. The formation of such complexes can alter the reactivity of the reagent molecules by changing their charge distribution or lowering the activation energy for subsequent reactions [13]. Since the reaction of isoprene and OH radicals is electrophilic, the isoprene-H_2O complex should have a different reactivity with respect to OH insertion, thereby influencing SOA formation to a large extent, due to the high abundance of isoprene and H_2O molecules in biogenic sources such as forests.

Intermolecular interactions between unsaturated hydrocarbon molecules and Lewis acids have been widely investigated experimentally [14–21] and theoretically [22–28], and it is well established that C=C double bonds act as proton acceptors. Thus, the concept of H—π H-bonds, which was proposed a long time ago [29], has been confirmed and typical examples of such bonding include C_2H_4-H_2O [15–17] and C_6H_6-H_2O [18–21]. Engdahl and Nelander extended the observation of these species in matrices [17,21] to other olefin-H_2O systems [30] and analogous gas-phase complexes with benzene derivatives have also been reported [31]. The interaction of isoprene and H_2O molecules, however, has not been reported to the best of our knowledge, and thus the structure of the isoprene-H_2O complex has remained unknown.

The purpose of the present study is to provide the first characterization of the isoprene-H_2O complex, from both experimental and computational aspects. A series of complexes was produced in cryogenic noble gas matrices, and their infrared spectra were compared with theoretical predictions from quantum chemical calculations to gain structural information on these species, following a successfully employed approach [32–36]. Finally, the relevance of the present study to atmospheric chemistry was addressed.

2. Experimental

Isoprene was purchased from Wako Pure Chemical Industry (Osaka, Japan), and used after degassing via freeze-pumpthaw cycles. Premixed samples of isoprene and H_2O were prepared by mixing the vapors and noble gas (Ar or Kr) at various ratios in a stainless steel vessel. Each gaseous sample was deposited onto a cold CsI surface maintained at 20 K for Ar and 25 K for Kr matrices.

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Other details of the experiments and instrumentation have been described elsewhere [32–36].

The spectra of the complexes obtained in Ar and Kr matrices are shown in Figs. 1 and 2, respectively. In reference to the recently reported infrared spectra [37], the absorption bands of isoprene are labeled with the designations of their vibrational modes. The peaks emerging with increasing water concentration can be assigned to the isoprene-H_2O complex, and are designated with asterisks (∗). Some of the vibrational peaks of the hydrate complex in the Ar matrix are bifurcated in contrast with those in Kr, which could be associated to multiple trapping sites in Ar, as has been previously observed [35–36].

The assignments of vibrational peaks of the complex were rather straightforward in fundamental bands of isoprene, while those in the O-H stretching region of H_2O required some consideration. Only one band was located in the Ar matrix, which was bifurcated to 3613 and 3616 cm^{-1}; this splitting was too small to allow assignment of the two fundamental bands. In addition, it was not certain whether this band should be assigned to the ν_1 or ν_3 of the H_2O moiety. On the other hand, a sharp peak at 3606 cm^{-1} and an additional broad band at 3657 cm^{-1} were observed in Kr. These bands were assigned to the ν_1 and ν_3 of H_2O, respectively. This allowed the bifurcated peaks at 3613 and 3616 cm^{-1} in Ar to be assigned to the ν_1 band. We assume that the bifurcated ν_3 band in the Ar matrix was obscured by the baseline noise and thus was not discernible. It should be noted that the ν_1 and ν_3 bands have comparable intensity in the isoprene-H_2O complex. This may be due to the change of charge distribution and vibrational intensity of the constituent molecule caused by H-bond formation. A similar intensity anomaly has been observed for C_6H_6-H_2O [19]. Further discussion will be made on this issue in a subsequent section for quantum chemical calculations.

The vibrational wavenumbers corresponding to each peak are presented in Table 1. The number in parenthesis is the wavenumber shift from the peak position of the corresponding isolated molecule. The peak position for each fundamental band of isoprene was taken from our recent study [37]. The rotationless band center for each of the ν_1/ν_3 bands in Ar was calculated by Michaut et al. [38], but the values for the bands in Kr have not been reported. We then approximately obtained the rotationless band centers as follows:

$$\omega_0(\nu_1) \sim (\omega(1_{1,0} \leftarrow 1_{0,1}) + \omega(1_{0,1} \leftarrow 1_{1,0}))/2 = 3628\ \mathrm{cm}^{-1} \qquad (1)$$

$$\omega_0(\nu_3) \sim (\omega(0_{0,0} \leftarrow 1_{0,1}) + \omega(1_{0,1} \leftarrow 0_{0,0}))/2 = 3724\ \mathrm{cm}^{-1} \qquad (2)$$

The position of each rovibrational line of H_2O in Kr was taken from Hirabayashi and Yamada [39].

3. Calculations

All calculations were done with the GAUSSIAN 09 [40] package. Three types of calculations were employed to locate stable isomers of the isoprene-H_2O complex: B3LYP [41–42] /6-31+G(2d,2p),

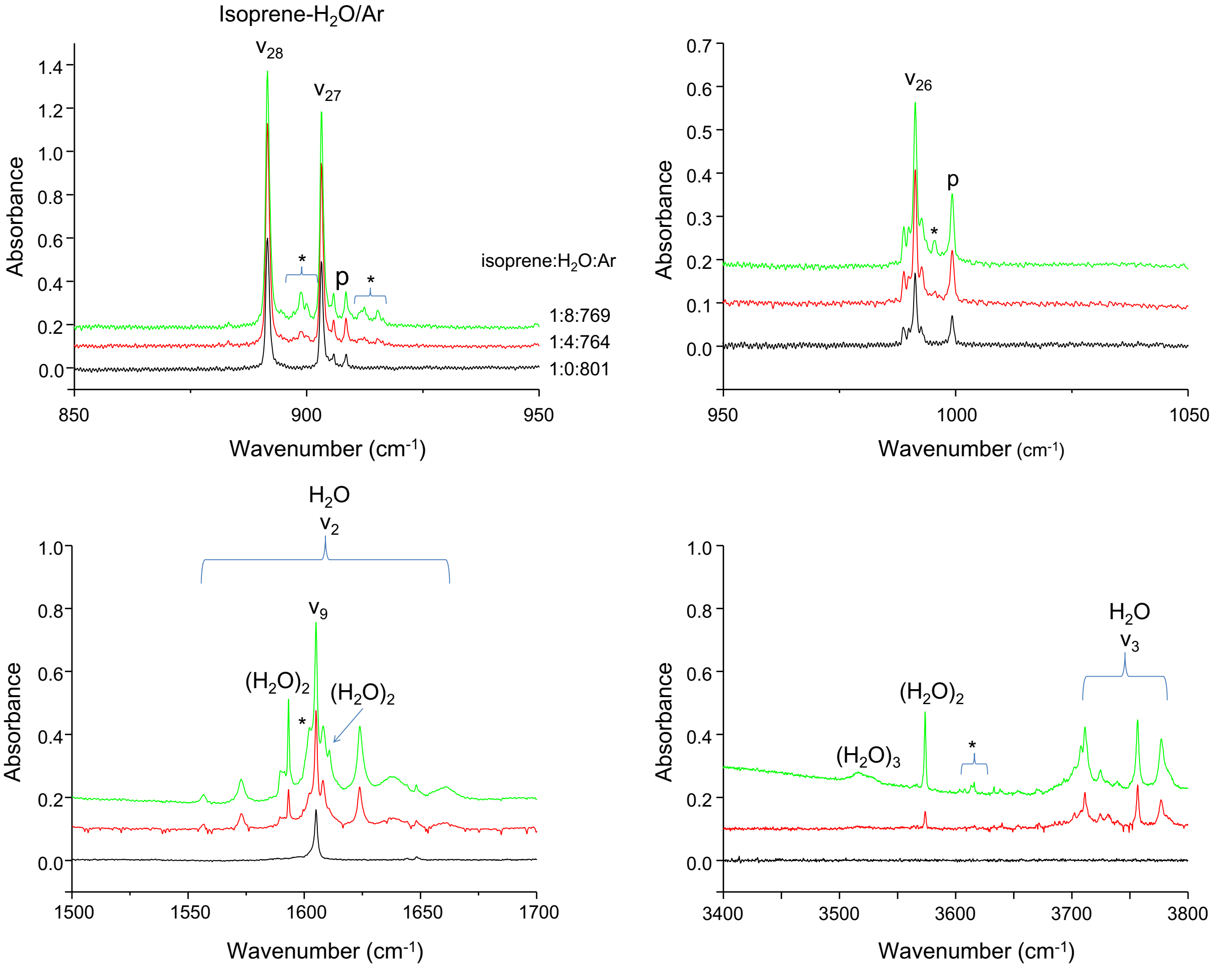

Fig. 1. Infrared spectra of the isoprene-H_2O complex in an Ar matrix. Vibrational bands of isoprene and H_2O are labeled with normal mode designations, and those of the complex are marked with asterisks (*). Peaks labeled with "p" are due to the polymeric species of isoprene.