

## ***Interactive comment on “Radiative effects of tropospheric ionisation” by K. L. Aplin***

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### **1. Introduction**

I thank the three referees for their very careful consideration of the paper and many helpful comments. As their general comments were similar, I will respond to them in one section. The specific comments of each referee are then considered separately.

### **2. Response to general comments**

The aim of this paper is to present evidence motivating further study of the infra-red (IR) absorption properties of molecular cluster-ions in the atmosphere. These cluster ions are formed by ionisation from cosmic rays and natural radioactivity and are principally composed of water ligands around a charged central molecule (which is often itself

a charged water molecule,  $H_3O^+$ ). Charged water clusters can also be formed by dissociation of neutral water clusters like dimers and trimers (Asmis et al., 2003). In the discussion paper it is suggested that IR absorption of molecular cluster-ions in atmospheric column concentrations may be detectable, and this may be relevant for studies of neutral clusters and the IR continuum. I am therefore encouraged that all the referees thought the effect described was plausible in the atmosphere, and potentially significant.

However it is important to note that whilst IR absorption from ions may *contribute* to the water vapour continuum absorption, ion concentrations in the atmosphere would never be high enough for ionic absorption to explain the whole water vapour continuum. Any absorption from cluster-ions or protonated oligomers is likely to be a small effect. Despite its small magnitude, the ionic absorption signal may be important, as there is evidence (Carlson and Harden, 1980; Asmis et al., 2003) that charged water clusters may be a proxy for water oligomers. The oligomers are abundant enough to account for the water vapour continuum absorption (Pfeilsticker et al., 2003; Evans and Vaida, 2000). Water oligomers are generally difficult to observe in the atmosphere because of the similarities between oligomer and monomer absorption bands (Pfeilsticker et al., 2003). Modern atmospheric ion measurement inversion techniques (Aplin and Harrison, 2001; Holden, 2003) could therefore potentially be used to detect variations in water oligomers. A further motivation to quantify the absorption signal of charged clusters is that the absorption changes, if poorly understood, could be spuriously attributed to other atmospheric species in satellite retrievals and radiative calculations. I agree that more detailed studies of all the aspects presented in the discussion paper are required to conclusively identify such an effect. The central purpose of this paper is merely to collate the evidence indicating that there may be a neglected atmospheric effect. Following the reassuring confirmation of this view from the referees' comments, this central point will be emphasised further in the revised version.

The referees also suggested that more detailed description of Carlson's measurements

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(e.g. Carlon and Harden, 1980; Carlon, 1982) and their application to the atmosphere would be appropriate. Consequently, in my revised manuscript, I will explain the methodology of applying the ion absorption cross-sections from analysis of Carlon's experiments to estimate the possible magnitude of an atmospheric effect. I concur entirely with the referees that a longer time series of atmospheric data is essential to fully establish statistical significance of the effect in an atmospheric data set. Consequently I have decided to remove the section and figure describing the atmospheric measurements and instead focus the paper on the atmospheric application of Carlon's experiments. (Experiments to gain more atmospheric data are now under way, and I hope to be able to report the results in a later publication.)

### 3. Response to specific comments

#### Referee #1

The referee doubted whether atmospheric concentrations of oligomers could be well known if the cross-sections are poorly understood. There are several estimates of oligomer concentrations in the atmosphere determined using different techniques, all of which are roughly consistent. For example Pfeilsticker et al. (2003) estimated atmospheric dimer concentrations of  $10^{14} \text{ cm}^{-3}$  using atmospheric long-path spectroscopy to search for absorption bands predicted by theory. In a theoretical paper, Headrick and Vaida (2001) calculate average atmospheric dimer concentrations to be  $10^{12} \text{ cm}^{-3}$  and trimer concentrations to be  $10^{10} \text{ cm}^{-3}$ . Vaida et al. (2001) estimated surface dimer concentrations from equilibrium constants to be  $10^{14} \text{ cm}^{-3}$  dropping to  $10^{10} \text{ cm}^{-3}$  at 10 km. It therefore does appear possible to obtain consistent oligomer concentration estimates even if cross-sections are not well known.

The exclusion of negative ions from the absorption calculations was not fully explained in the discussion paper. The water cluster ion or protonated water oligomer

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$H_3O^+(H_2O)_n$  is one of the most common tropospheric positive ion species (e.g. Harrison and Carslaw, 2003), and is known to absorb in the IR (e.g. Carlon and Harden, 1982; Asmis et al., 2003). However, almost all atmospheric small ions are clustered with water to some extent, and could therefore absorb in the IR via rotational-vibrational transitions of the hydrogen bonds, similar to the absorption mechanism in neutral and charged water clusters (e.g. Pfeilsticker et al., 2003; Asmis et al., 2003). Model calculations suggest that the most common ligands for negative tropospheric ions are nitric and sulphuric acid (Beig and Brasseur, 2000). This implies that positive ions, which are more commonly clustered with hydrogen bonded water molecules, may interact preferentially with IR radiation. Yet many common negative ion species are clustered with water e.g.  $O_2^-(H_2O)_n$  and  $CO_3^-(H_2O)_n$ , and some abundant positive ion species are not completely clustered with water e.g.  $H^+(NH_3)_x(pyridine)(H_2O)_n$  (Harrison and Carslaw, 2003). It is therefore conservative to totally ignore the contribution of negative ions to IR absorption, as in the discussion paper. As not all positive ions are likely to contribute to IR absorption, it appears reasonable to balance these two assumptions by basing the ion column concentration calculations on the total positive ion concentration, roughly half the ions present in the atmosphere. I agree with the referee that a profile of the ion concentration would be helpful, and this will be added to the revised manuscript, along with further details on the assumptions made about atmospheric ion composition.

Carlon's measurements were carried out at typical atmospheric saturations of 0.4 to 0.8 and at atmospheric pressure in the temperature range 24–27°C. Absorption cross sections  $\alpha$  derived from these measurements therefore seem applicable to atmospheric absorption. I thank the referee for pointing out the error in the calculation of transmissivity from in equations (6) and (7). These will be replaced by equation (1) below in the revised version of the paper, where a layer model will be used to estimate the transmissivity at the surface for a standard atmosphere with density  $\rho$  from an atmospheric column of ions up to height  $z$ , with  $\alpha$  a function of wavelength  $\lambda$  and ion concentration

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$n$ .

$$\frac{I}{I_0}(\lambda) = \exp\left(-\int_0^z \alpha(\lambda, n)\rho dz\right). \quad (1)$$

The referee criticised the “very, very rough estimate” made using a very simplistic isothermal model. This was intended to be an order of magnitude estimate for the possible atmospheric signal of molecular cluster-ion absorption. The use of an integrated columnar absorption, as suggested by the referee, in the revised version should improve estimates of the magnitude of a possible atmospheric signal.

## Referee #2

I am grateful to the referee for identifying where more clarity is needed in describing the cross-sections used in the discussion paper. Carlon’s measurements were carried out in humid air with large concentrations of ions present, so the cross-sections he presents are due to a combination of water cluster-ions and neutral water vapour. If cross-section is plotted as a function of ion concentration, it shows a linear relationship with a non-zero offset. It is likely that this background absorption is caused by the water vapour also present in Carlon’s measurements. The presence of water vapour absorption bands at very similar wavelengths to those used by Carlon (Rothman et al., 1998) supports this, and justifies the approach taken. The sensitivity of cross-section to ion concentration is given by the gradient of the best-fit line to the data points obtained by Carlon under atmospheric conditions. This will be explained more clearly in the revised version.

The referee suggested that ion-induced nucleation could cause an absorption signal in atmospheric observations of IR attenuation. This is possible, as molecular cluster-ions may contribute to particle formation in the atmosphere, (Yu and Turco, 2001) which could interact with IR radiation in addition to the hydrogen bond interactions expected from the charged clusters. The revised version will include more detailed estimates

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of the atmospheric IR absorption expected from molecular cluster-ions. This should assist in identifying any additional absorption from ion-induced atmospheric aerosol formation in future atmospheric observations.

### Referee #3

The referee correctly points out that path lengths are required to estimate the magnitude of the absorption in the atmosphere. The aim of Section 3 was to compare the possible relative contributions of neutral and charged clusters to the IR continuum absorption, over a constant column height. This is why typical concentrations were given rather than column content, however column content may be more appropriate for a discussion of absorption, and will be added to Section 3.

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