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ARTICLE in CHEMICAL PHYSICS LETTERS · OCTOBER 1997

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## Infrared predissociation spectra of $\text{He-HO}_2^+$ and $\text{Ne-HO}_2^+$ : prediction of the $\nu_1$ frequency of $\text{HO}_2^+$

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Received 16 July 1997

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### Abstract

Infrared spectra of the  $\nu_1$  vibration (O–H stretch) of the proton-bound  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  ionic complexes have been obtained by means of photodissociation spectroscopy in a tandem mass spectrometer. The measured vibrational frequencies of 2905 and 2761  $\text{cm}^{-1}$  allow for an estimation of the unknown  $\nu_1$  frequency of the  $\text{HO}_2^+$  monomer as  $3020 \pm 40 \text{ cm}^{-1}$ . © 1997 Elsevier Science B.V.

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### 1. Introduction

Matrix isolation methods have been used extensively in the past to study the spectroscopy of transient and reactive species [1]. Often these data provide help in the observation of the corresponding gas-phase absorptions by localizing the wavelength range for the search. In the gas phase, the species of interest can be surrounded by one or more solvent atoms or molecules to form a cluster, whereby its spectroscopic properties will sensitively depend on number and nature of the attached ligands. For example, such a ‘messenger’ technique has been applied to complexes of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  with hydrogen and neon in order to locate approximately the high-frequency vibrations of the protonated water clusters via predissociation spectroscopy [2]. In the present study, a similar strategy is exploited to set relatively narrow limits for the spectral position of the OH stretching vibration ( $\nu_1$ ) of  $\text{HO}_2^+$ , an ion which has

so far eluded high-resolution spectroscopists [3]. Despite its relevance in the chemistry of combustion processes, oxygen and hydrogen containing plasmas, and the ionosphere [4,5], of its three fundamental frequencies only the O–O stretching vibration ( $\nu_2$ ) is approximately known from photoelectron spectroscopic studies, with a harmonic frequency of  $1560 \pm 50 \text{ cm}^{-1}$  [6]. In the present study the frequency of the O–H stretching vibration ( $\nu_1$ ) of  $\text{HO}_2^+$  is inferred from the spectra of its complexes with the rare gas (Rg) atoms He and Ne.

There have been several theoretical studies dealing with the structure and vibrational frequencies of  $\text{HO}_2^+$ ; see for example Ref. [5]. The ion is calculated to be bent by about  $112^\circ$  in the  $^3A'$  ground electronic state. Probably the best theoretical predictions for the frequencies of the three fundamentals, corrected for anharmonic effects, are  $\nu_1 = 3140 \pm 100 \text{ cm}^{-1}$ ,  $\nu_2 = 1535 \pm 40 \text{ cm}^{-1}$ , and  $\nu_3 = 1140 \pm 40 \text{ cm}^{-1}$  [5]. Ho et al. [3] have conducted a search for the  $\nu_1$  transition of  $\text{HO}_2^+$  in an  $\text{O}_2/\text{H}_2/\text{He}$  discharge in the spectral range between 3100 and  $3600 \text{ cm}^{-1}$ , but

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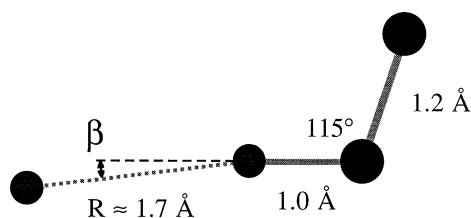


Fig. 1. Approximate structure of  $\text{Rg-HO}_2^+$  complexes ( $\text{Rg} = \text{He/Ne}$ ) derived from comparison with the calculated structure of  $\text{H}_2\text{-HO}_2^+$  [7]. The angle  $\beta$  is believed to be significantly smaller than  $10^\circ$ .

could only identify strong absorptions arising from  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ . The complexes between a  $\text{Rg}$  atom and the  $\text{HO}_2^+$  ion have not been characterized either theoretically or experimentally. However, the structure of the closely related  $\text{H}_2\text{-HO}_2^+$  complex has been investigated by ab initio methods [7]. It was found that the structural parameters of  $\text{HO}_2^+$  remain

fairly undistorted in the complex. The  $\text{H}_2$  ligand is weakly attached to the proton side of  $\text{HO}_2^+$  to form a planar nearly T-shaped complex. There is a small angle  $\beta$  ( $10^\circ$ ) between the OH bond and the line joining the central proton and the midpoint of the  $\text{H}_2$  moiety resulting from the repulsive interaction with the oxygen atoms. The degree of monomer distortion and the angle  $\beta$  are expected to be significantly smaller in the less strongly bound complexes  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  investigated in the present work. The minimum energy structure of these complexes is therefore believed to correspond closely to the one shown in Fig. 1.

## 2. Experimental

The spectra of the complexes  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  displayed in Fig. 2 were obtained by infrared (IR) photodissociation spectroscopy in a tandem mass spectrometer described in detail elsewhere [8,9]. The technique relies on photoexcitation of the mass selected complexes to predissociating states, and monitoring the dissociation yield as a function of the excitation frequency. The complexes were produced in an electron impact-supersonic expansion ion source. A mixture of  $\text{He}(\text{Ne})$ ,  $\text{O}_2$ , and  $\text{H}_2$  with a ratio of 100:1:1 at 6–8 bar was used to prepare the complexes. The current of the  $\text{HO}_2^+$  ions was under any conditions a factor of 5–10 smaller than that of  $\text{O}_2^+$  or  $\text{H}_3\text{O}^+$ . Calibration of the tunable IR light source, an OPO laser system with  $0.02\text{ cm}^{-1}$  bandwidth, was accomplished by recording optoacoustic spectra of HDO [10].

## 3. Results and discussion

The photodissociation spectra of  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  shown in Fig. 2 correspond to the region of the intramolecular OH stretching vibration ( $\nu_1$ ) of  $\text{HO}_2^+$ . No other bands have been detected for  $\text{He-HO}_2^+$  between 2700 and  $3400\text{ cm}^{-1}$  and for  $\text{Ne-HO}_2^+$  between 2500 and  $2950\text{ cm}^{-1}$ . Consequently, the most intense bands in the spectra of Fig. 2, observed near 2905 and  $2760\text{ cm}^{-1}$ , are assigned to the  $\nu_1$  fundamentals of the  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  complexes, respectively. It is noted that the overtone

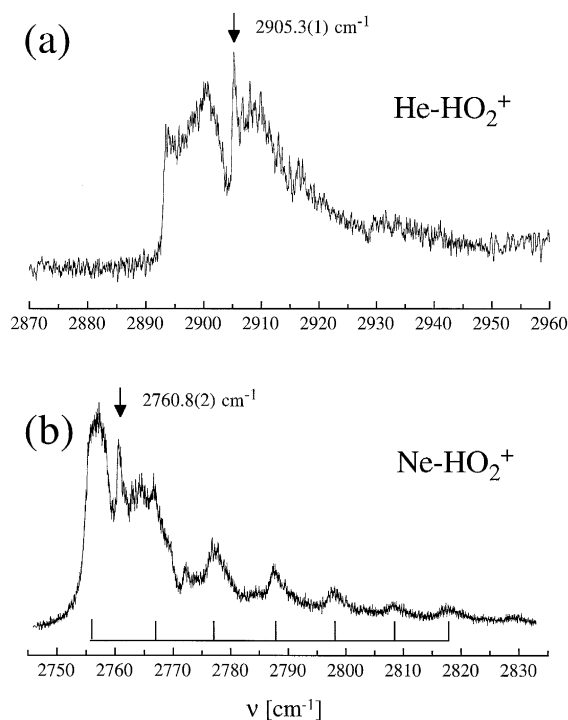


Fig. 2. Infrared predissociation spectra of mass-selected  $\text{He-HO}_2^+$  (a) and  $\text{Ne-HO}_2^+$  (b) complexes recorded in the  $\text{HO}_2^+$  fragment channel. The arrows mark the position of the Q branches of the respective  $\nu_1$  bands. The spectrum of  $\text{Ne-HO}_2^+$  contains unassigned sequence transitions indicated by the comb.

of the  $\nu_2$  vibration of  $\text{HO}_2^+$  ( $1560 \pm 50 \text{ cm}^{-1}$  [6]) is expected to lie also in the considered spectral region; however, the IR intensity of this fundamental is calculated to be about two orders of magnitude smaller than that of the  $\nu_1$  vibration [5].

Individual rotational lines of the  $\nu_1$  transition are not resolved in the spectra of either complex; however, the band contours are readily discernible. The lack of rotational structure cannot be attributed solely to the limited resolution of the IR laser ( $0.02 \text{ cm}^{-1}$ ) or poor signal-to-noise ratio. Simulations based on geometries similar to those shown in Fig. 1 suggest that rotational structure should be easily resolved, at least for the lighter  $\text{He-HO}_2^+$  complex. Assuming that the rotational structure is washed out by homogeneous line broadening due to rapid predissociation, the lifetime of the  $\nu_1$  state can be estimated to be shorter than a few picoseconds for both complexes.

A closer look at the band profiles reveals moderately sized Q branches near the center of both transitions, with measured frequencies of  $2905.3(1)$  and  $2760.8(2) \text{ cm}^{-1}$  for  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$ , respectively. The observed contours are consistent with a bent asymmetric structure of the complexes and the transition dipole moment directed slightly away from the molecular axis. The P branches of the bands are degraded suggesting that the complexes are more compact in the vibrationally excited state, as is typical for proton-bound species of this kind [11–13]. The general features of the transitions can be reproduced using a structure similar to that in Fig. 1 for the ground state and small positive values for  $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ , indicating that the intermolecular bond strengths increase upon vibrational excitation. However, the population distribution of the rotational energy levels in the vibrational ground state seems to deviate substantially from an equilibrium situation rendering a quantitative description of the band profiles rather difficult.

A series of regularly spaced features to the blue of the  $\nu_1$  band in the spectrum of  $\text{Ne-HO}_2^+$  is associated with P branches of sequence bands  $\nu_1 + \nu_x - \nu_x$ , where  $\nu_x$  represents intermolecular vibration(s). Such sequence bands are expected to be shifted to the blue of the  $\nu_1$  transition due to the stronger intermolecular interaction in the  $\nu_1$  excited state. The spectra of  $\text{Ne-HN}_2^+$  and  $\text{Ne-HCO}^+$  [12] also feature a relatively high activity of hot bands. The reason for poor

vibrational cooling in the Ne-based discharges remains, however, obscure.

The band centers of the  $\nu_1$  vibrations of  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  are displaced from the yet unknown transition of the free  $\text{HO}_2^+$  ion by an amount characteristic for each complex, defined as the red shift in the frequency of the OH vibration ( $\Delta\nu_1$ ). The presence of the Rg ligand tends to reduce the potential energy of the system near the outer turning point of the OH vibration due to a partial proton transfer. This has the net effect of increasing the anharmonic contributions to the effective potential and thus reducing the  $\nu_1$  vibrational frequency. If the complex is sufficiently weakly bound, the complex's constituents conserve their individual properties and the red shift can be viewed as the difference in the well depths of the vibrationally averaged potentials for the intermolecular interaction between the Rg atom and the  $\text{HO}_2^+$  ion in the  $\nu_1 = 1$  and  $\nu_1 = 0$  states [14].

For the complexes  $\text{He-HN}_2^+$  [11] and  $\text{Ne-HCO}^+$  [12] it was shown that the attractive part of the intermolecular potential is governed by inductive forces which are in turn dominated by the charge-induced dipole interaction. In addition, the intermolecular separations ( $R_{\text{Rg-H}}$ ) in the  $\text{Rg-HCO}^+$  and  $\text{Rg-HN}_2^+$  complexes (Rg = He, Ne) are nearly independent of the Rg ligand, being roughly  $2.0 \text{ \AA}$  in the former and  $1.7\text{--}1.8 \text{ \AA}$  in the latter series. Assuming that the difference in the binding energy of such a complex in the  $\nu_1 = 1$  and  $\nu_1 = 0$  states arises from the reorganization of the charge distribution in the ion caused by the excitation of the XH vibration (X = N, C, O in case of  $\text{HN}_2^+$ ,  $\text{HCO}^+$ ,  $\text{HO}_2^+$ , respectively), the red shift can be correlated with the volume polarizability of the rare gas. Fig. 3 displays the frequencies of the  $\nu_1$  vibrations in the complexes of  $\text{HN}_2^+$ ,  $\text{HCO}^+$ , and  $\text{HO}_2^+$  with He and Ne as a function of the ligand polarizability (Table 1). It is found that the frequencies of free  $\text{HCO}^+$  and  $\text{HN}_2^+$  can be predicted more or less accurately by linear extrapolation of the  $\text{Rg-HN}_2^+$  and  $\text{Rg-HCO}^+$  data. The predicted frequencies are overestimated by only 0.6 and 1.1%, respectively. Proceeding in a similar way, an upper limit for the  $\nu_1$  frequency of  $\text{HO}_2^+$  can be estimated as  $3060 \text{ cm}^{-1}$  based on the  $\text{He-HO}_2^+$  and  $\text{Ne-HO}_2^+$  data (Fig. 3). Assuming that this value exaggerates the real frequency of this vibration

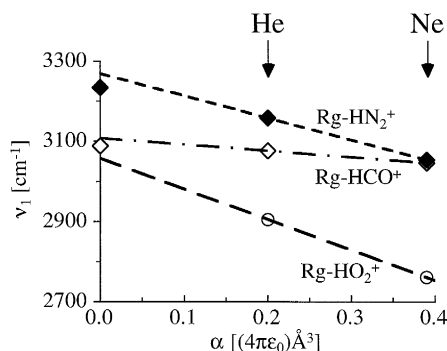


Fig. 3. Estimation of the frequency of the  $\nu_1$  vibration of  $\text{HO}_2^+$  from the proposed correlation between polarizabilities  $\alpha$  of the rare gas (0.20 and  $0.39 \text{ } 4\pi\epsilon_0 \text{ \AA}^3$  for He and Ne, respectively [19]) and  $\nu_1$  red shifts in complexes  $\text{Rg-HX}^+$ , where  $\text{X} = \text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}$ , and  $\text{Rg} = \text{He}$  and  $\text{Ne}$ . Because the frequencies of the  $\text{HCO}^+$  and  $\text{HN}_2^+$  monomers are overestimated somewhat by this method, the intercept of the lowest line at  $\approx 3060 \text{ cm}^{-1}$  is believed to provide an upper limit for  $\nu_1$  of  $\text{HO}_2^+$ .

also by about 0.6–1.1% leads to an estimation of  $\nu_1$  as  $3020\text{--}3040 \text{ cm}^{-1}$ .

A lower limit for the  $\nu_1$  frequency of  $\text{HO}_2^+$  can be obtained from another simple comparison. In the series of proton-bound complexes  $\text{He-HX}^+$ , the influence of the He ligand on the frequency of the  $\text{HX}$  vibration is expected to be larger for bases  $\text{X}$  with lower proton affinity  $\text{PA}_\text{X}$ . The frequency drops by more than 50% in the symmetric complex  $\text{He-H-He}^+$  [15], whereas it barely changes in  $\text{He-HCO}^+$  ( $\Delta\nu_1 = 12 \text{ cm}^{-1}$  [13]). As molecular oxygen possesses a somewhat lower proton affinity than molecular nitrogen ( $\text{PA}_{\text{CO}} = 594 \text{ kJ/mol}$ ;  $\text{PA}_{\text{N}_2} = 495 \text{ kJ/mol}$ ;  $\text{PA}_{\text{O}_2} = 420 \text{ kJ/mol}$ ;  $\text{PA}_{\text{He}} = 127 \text{ kJ/mol}$  [16,17]), it is expected that the red shift in the  $\text{He-HO}_2^+$  complex is at least as great as in  $\text{He-HN}_2^+$  where it amounts to 2.4% ( $\Delta\nu_1 = 75.5 \text{ cm}^{-1}$  [18]). Thus, a lower limit for the  $\nu_1$  frequency of  $\text{HO}_2^+$  can be derived as  $2980 \text{ cm}^{-1}$ . In general the

increase in the proton affinity of  $\text{X}$  ( $\text{PA}_{\text{O}_2} < \text{PA}_{\text{N}_2} < \text{PA}_{\text{CO}}$ ) results in a weaker intermolecular bond strength in the respective  $\text{Rg-HX}^+$  complexes and thus in a smaller complexation induced  $\nu_1$  red shift (as indicated by the different slopes of the curves in Fig. 3).

#### 4. Conclusion

The frequency of the  $\nu_1$  vibration of  $\text{HO}_2^+$  has been bracketed to  $2980\text{--}3060 \text{ cm}^{-1}$ , by comparing  $\nu_1$  red shifts in the set of related proton-bound complexes of  $\text{HO}_2^+$ ,  $\text{HN}_2^+$ , and  $\text{HCO}^+$  with He and Ne. If this prediction is correct, the ab initio frequency of  $3140 \pm 100 \text{ cm}^{-1}$  [5] appears to be somewhat too high. The specified range has not been covered in the search for the  $\nu_1$  band of  $\text{HO}_2^+$  by Ho et al. [3] which may explain the lack of detection of IR absorptions of this ion in the  $\text{O}_2/\text{H}_2/\text{He}$  discharge. It is hoped that the derived prediction for the  $\nu_1$  fundamental will stimulate further spectroscopic work on this interesting ion.

#### Acknowledgements

This study is part of the project No. 20-49104.96 of the Swiss National Science Foundation.

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Table 1

Frequency (in  $\text{cm}^{-1}$ ) of the  $\nu_1$  vibration of selected  $\text{HX}^+$  ions and their complexes with He and Ne

	$\text{X} = \text{CO}$	$\text{X} = \text{N}_2$	$\text{X} = \text{O}_2$
$\text{HX}^+$	3088.7 <sup>a</sup>	3234.0 <sup>d</sup>	
$\text{He-HX}^+$	3076.3 <sup>b</sup>	3158.4 <sup>e</sup>	2905.3
$\text{Ne-HX}^+$	3046.1 <sup>c</sup>	3053.5 <sup>f</sup>	2760.8

<sup>a</sup>Ref. [20]; <sup>b</sup>Ref. [13]; <sup>c</sup>Ref. [12]; <sup>d</sup>Ref. [21]; <sup>e</sup>Ref. [11]; <sup>f</sup>Ref. [22].

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