

Infrared predissociation spectra of He–HO₂⁺ and Ne–HO₂⁺: prediction of the ν_1 frequency of HO₂⁺

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Abstract

Infrared spectra of the ν_1 vibration (O–H stretch) of the proton-bound He–HO₂⁺ and Ne–HO₂⁺ ionic complexes have been obtained by means of photodissociation spectroscopy in a tandem mass spectrometer. The measured vibrational frequencies of 2905 and 2761 cm⁻¹ allow for an estimation of the unknown ν_1 frequency of the HO₂⁺ monomer as 3020 ± 40 cm⁻¹. © 1997 Elsevier Science B.V.

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 H₃O⁺–(H₂O)_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 (ν_1) of HO₂⁺, 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 (ν_2) is approximately known from photoelectron spectroscopic studies, with a harmonic frequency of 1560 ± 50 cm⁻¹ [6]. In the present study the frequency of the O–H stretching vibration (ν_1) of HO₂⁺ 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 HO₂⁺; see for example Ref. [5]. The ion is calculated to be bent by about 112° in the ³A' ground electronic state. Probably the best theoretical predictions for the frequencies of the three fundamentals, corrected for anharmonic effects, are $\nu_1 = 3140 \pm 100$ cm⁻¹, $\nu_2 = 1535 \pm 40$ cm⁻¹, and $\nu_3 = 1140 \pm 40$ cm⁻¹ [5]. Ho et al. [3] have conducted a search for the ν_1 transition of HO₂⁺ in an O₂/H₂/He discharge in the spectral range between 3100 and 3600 cm⁻¹, but

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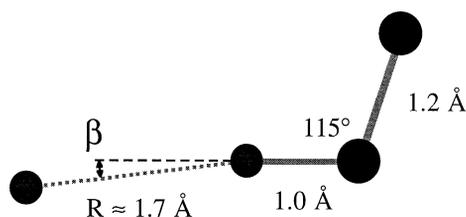


Fig. 1. Approximate structure of $Rg-HO_2^+$ complexes ($Rg = He/Ne$) derived from comparison with the calculated structure of $H_2-HO_2^+$ [7]. The angle β is believed to be significantly smaller than 10° .

could only identify strong absorptions arising from H_2O^+ and H_3O^+ . The complexes between a Rg atom and the HO_2^+ ion have not been characterized either theoretically or experimentally. However, the structure of the closely related $H_2-HO_2^+$ complex has been investigated by ab initio methods [7]. It was found that the structural parameters of HO_2^+ remain

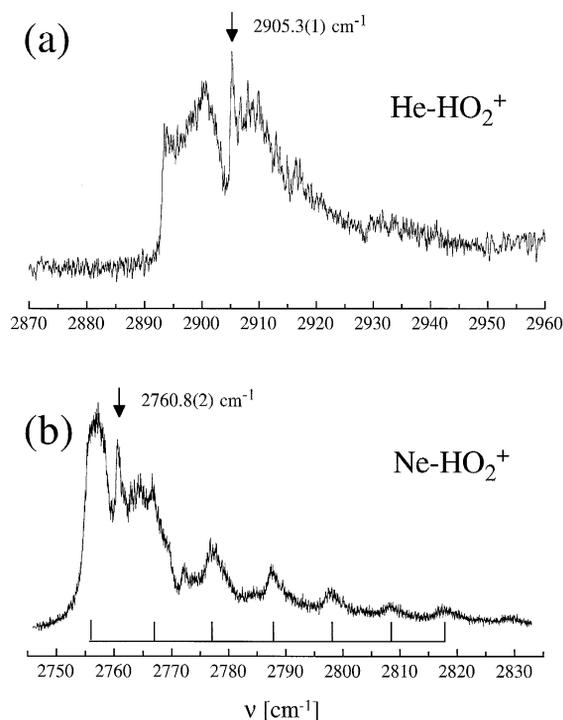


Fig. 2. Infrared predissociation spectra of mass-selected $He-HO_2^+$ (a) and $Ne-HO_2^+$ (b) complexes recorded in the HO_2^+ fragment channel. The arrows mark the position of the Q branches of the respective ν_1 bands. The spectrum of $Ne-HO_2^+$ contains unassigned sequence transitions indicated by the comb.

fairly undistorted in the complex. The H_2 ligand is weakly attached to the proton side of HO_2^+ to form a planar nearly T-shaped complex. There is a small angle β (10°) between the OH bond and the line joining the central proton and the midpoint of the H_2 moiety resulting from the repulsive interaction with the oxygen atoms. The degree of monomer distortion and the angle β are expected to be significantly smaller in the less strongly bound complexes $He-HO_2^+$ and $Ne-HO_2^+$ 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 $He-HO_2^+$ and $Ne-HO_2^+$ 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 $He(Ne)$, O_2 , and H_2 with a ratio of 100:1:1 at 6–8 bar was used to prepare the complexes. The current of the HO_2^+ ions was under any conditions a factor of 5–10 smaller than that of O_2^+ or H_3O^+ . Calibration of the tunable IR light source, an OPO laser system with 0.02 cm^{-1} bandwidth, was accomplished by recording optoacoustic spectra of HDO [10].

3. Results and discussion

The photodissociation spectra of $He-HO_2^+$ and $Ne-HO_2^+$ shown in Fig. 2 correspond to the region of the intramolecular OH stretching vibration (ν_1) of HO_2^+ . No other bands have been detected for $He-HO_2^+$ between 2700 and 3400 cm^{-1} and for $Ne-HO_2^+$ between 2500 and 2950 cm^{-1} . Consequently, the most intense bands in the spectra of Fig. 2, observed near 2905 and 2760 cm^{-1} , are assigned to the ν_1 fundamentals of the $He-HO_2^+$ and $Ne-HO_2^+$ complexes, respectively. It is noted that the overtone

of the ν_2 vibration of 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 ν_1 vibration [5].

Individual rotational lines of the ν_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 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 He-HO_2^+ complex. Assuming that the rotational structure is washed out by homogeneous line broadening due to rapid predissociation, the lifetime of the ν_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 He-HO_2^+ and 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 ΔA , ΔB , and ΔC , 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 ν_1 band in the spectrum of Ne-HO_2^+ is associated with P branches of sequence bands $\nu_1 + \nu_x - \nu_x$, where ν_x represents intermolecular vibration(s). Such sequence bands are expected to be shifted to the blue of the ν_1 transition due to the stronger intermolecular interaction in the ν_1 excited state. The spectra of Ne-HN_2^+ and 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 ν_1 vibrations of He-HO_2^+ and Ne-HO_2^+ are displaced from the yet unknown transition of the free 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 ν_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 HO_2^+ ion in the $\nu_1 = 1$ and $\nu_1 = 0$ states [14].

For the complexes He-HN_2^+ [11] and 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 Rg-HCO^+ and Rg-HN_2^+ complexes (Rg = He, Ne) are nearly independent of the Rg ligand, being roughly 2.0 \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 HN_2^+ , HCO^+ , HO_2^+ , respectively), the red shift can be correlated with the volume polarizability of the rare gas. Fig. 3 displays the frequencies of the ν_1 vibrations in the complexes of HN_2^+ , HCO^+ , and HO_2^+ with He and Ne as a function of the ligand polarizability (Table 1). It is found that the frequencies of free HCO^+ and HN_2^+ can be predicted more or less accurately by linear extrapolation of the Rg-HN_2^+ and 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 ν_1 frequency of HO_2^+ can be estimated as 3060 cm^{-1} based on the He-HO_2^+ and Ne-HO_2^+ data (Fig. 3). Assuming that this value exaggerates the real frequency of this vibration

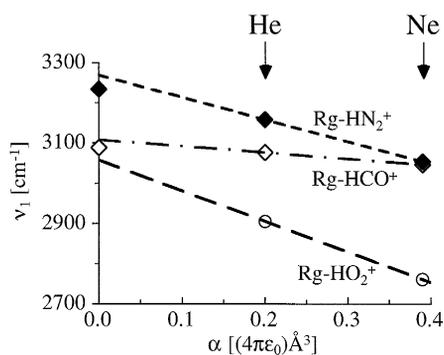


Fig. 3. Estimation of the frequency of the ν_1 vibration of HO_2^+ from the proposed correlation between polarizabilities α of the rare gas (0.20 and $0.39 \text{ } 4\pi\epsilon_0 \text{ \AA}^3$ for He and Ne, respectively [19]) and ν_1 red shifts in complexes Rg-HX^+ , where $\text{X} = \text{O}_2, \text{N}_2,$ and CO , and $\text{Rg} = \text{He}$ and Ne . Because the frequencies of the HCO^+ and 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 ν_1 of HO_2^+ .

also by about 0.6–1.1% leads to an estimation of ν_1 as $3020\text{--}3040 \text{ cm}^{-1}$.

A lower limit for the ν_1 frequency of HO_2^+ can be obtained from another simple comparison. In the series of proton-bound complexes He-HX^+ , the influence of the He ligand on the frequency of the HX vibration is expected to be larger for bases X with lower proton affinity PA_X . The frequency drops by more than 50% in the symmetric complex He-H-He^+ [15], whereas it barely changes in 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 He-HO_2^+ complex is at least as great as in He-HN_2^+ where it amounts to 2.4% ($\Delta\nu_1 = 75.5 \text{ cm}^{-1}$ [18]). Thus, a lower limit for the ν_1 frequency of HO_2^+ can be derived as 2980 cm^{-1} . In general the

Table 1
Frequency (in cm^{-1}) of the ν_1 vibration of selected HX^+ ions and their complexes with He and Ne

	X = CO	X = N ₂	X = O ₂
HX^+	3088.7 ^a	3234.0 ^d	
He-HX^+	3076.3 ^b	3158.4 ^c	2905.3
Ne-HX^+	3046.1 ^c	3053.5 ^f	2760.8

^aRef. [20]; ^bRef. [13]; ^cRef. [12]; ^dRef. [21]; ^eRef. [11]; ^fRef. [22].

increase in the proton affinity of 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 Rg-HX^+ complexes and thus in a smaller complexation induced ν_1 red shift (as indicated by the different slopes of the curves in Fig. 3).

4. Conclusion

The frequency of the ν_1 vibration of HO_2^+ has been bracketed to $2980\text{--}3060 \text{ cm}^{-1}$, by comparing ν_1 red shifts in the set of related proton-bound complexes of HO_2^+ , HN_2^+ , and 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 ν_1 band of 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 ν_1 fundamental will stimulate further spectroscopic work on this interesting ion.

Acknowledgements

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