symmetry was relaxed, however, both the rectangular and diamond structures reached convergence. The energy was slightly lower in the B_{2g} structure for the singlet state, but the order was reversed for the triplet state (Table I). A similar situation was encountered in the investigation of Jahn-Teller distortions of the methane cation.⁵⁷ This bifurcation of available distortion coordinates, which was not encountered in the ZnTFP calculation, may relate to the instability of the A_{1u} cation radical to distortion. Because the A_{1u} cation is bond alternant, however, neither the B_{1g} nor the B_{2g} excited-state structure resembles the resultant of radical-cation and -anion structures. Relative to the ZnTFP excited states, the B_{1g} states of ZnP show a more even expansion and contraction of the $C_{\alpha}C_{m}$ and ZnN bonds and a reversal in the net contraction and expansion of the $C_{\alpha}C_{\beta}$ and $C_{\beta}C_{\beta}$ bonds. For this reason, a number of vibrational modes, e.g., ν_2 , ν_4 , ν_{10} , ν_{12} , ν_{19} , and ν_{29} , are predicted to shift in a direction opposite to ZnTFP, when force constant scaling is applied (Table V). The B_{2g} state involves expansion of the $C_{\alpha}N$ and $C_{\alpha}C_{\beta}$ bonds on one side of each pyrrole ring and contraction on the other, with little change in the $C_{\beta}C_{\beta}$ or $C_{\alpha}C_{m}$ bonds. Surprisingly, however, the calculated vibrational frequency changes are not very different for the B_{1g} and B_{2g} states (Table V). As in the case of ZnTFP, the bond distance changes for the singlet states are in the same direction but are smaller than for the triplet states.

Conclusions

MNDO/3 satisfactorily calculates the geometry and frontier orbital coefficients of zinc porphine. Substituting F for H at the meso positions has the effect of driving the a_{2u} orbital above the a_{1u} orbital. Extraction of an electron from ZnTFP is calculated

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to produce an expansion of the $C_a C_m$ and $C_\beta C_\beta$ bonds and of the core size and a contraction of the $C_\alpha C_\beta$ bonds, as expected from the a_{2u} orbital pattern. Extraction of an electron from ZnP, however, is calculated to produce a marked alternation of the $C_{\alpha}C_{m}$ bonds, in striking agreement with crystallographic evidence that OEP (A_{1u} ground state) but not TPP (A_{2u} ground state) undergoes a bond alternant distortion in the radical cation. This difference is suggested to arise from the sensitivity of the A_{1u} ground state to mixing with the A_{2u} excited state via an A_{2g} distortion, because of the a_{1u} nodes at the C_m and N atoms. Calculation of the vibrational frequencies using force constant scaling to the calculated bond distance changes reproduces the distinctive up and down shifts for A_{1u} and A_{2u} radical cations of the ν_2 marker band. The observed A_{1u} shift pattern of several modes is satisfactorily calculated with this method, but the A_{2u} shifts, other than v_2 , are in disagreement with experiment, suggesting a need to reexamine the assignments and/or the normal-mode compositions. The radical anion of ZnP and the singlet and triplet excited states of both porphyrins are calculated to undergo a B_{1g} distortion, in agreement with EPR analyses of porphyrin anion and triplet states. The TPP anion and triplet downshifts in ν_2 are also calculated correctly by the force constant scaling procedure, but it fails for the J-T-active B_{1g} and B_{2g} modes. The excited-state B_{1g} distortion is calculated to be different in form for ZnP and ZnTFP, due to the different orbital configurations. An energetically accessible B_{2g} -distorted excited state is found for ZnP, but not for ZnTFP. In all cases, the singlet excited states are determined to have the same shapes as the corresponding triplet states, with smaller net bond length changes, consistent with quenching of the Jahn-Teller effect due to orbital mixing when the symmetry is lowered.

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Fourier-Transform IR Spectroscopic Observation of Gaseous Nitrosyl Iodine, Nitryl Iodine, and Iodine Nitrate

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Using the photolysis of $I_2-NO_x-N_2$, mixtures the nitrogen oxylodines nitrosyl iodine (INO), nitryl iodine (INO₂), and iodine nitrate (IONO₂) have been produced in situ in the gas phase in a large glass reaction chamber and their infrared absorption spectra were recorded in the range 600-4000 cm⁻¹ at 298 ± 2 K. This is the first report of the IR gas-phase spectra of these compounds and also the very first report of the IR spectrum of IONO₂. IONO₂ was observed to decay in the dark with a first-order rate coefficient of $\sim 3.2 \times 10^{-2} \text{ s}^{-1}$ under the experimental conditions of the study. Although it is not clear if the decay is due entirely to thermal decay, it is much higher than the value generally used in model simulations of iodine chemistry in the troposphere; repercussions for the atmospheric iodine cycle are briefly discussed. Nitrogen pentoxide (N₂O₅) was also a product in the I₂-NO₂-N₂ photolysis system used to produce IONO₂. The formation of N₂O₅ is thought to involve the photolysis of IONO₂ to give NO₃ radicals, which with NO₂ rapidly establish an equilibrium with N₂O₅:

$$IONO_2 + h\nu \rightarrow I + NO_3$$

 $NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$

The possible use of this system as a continuous source of NO₃ radicals for laboratory experiments is also considered.

1. Introduction

There has recently been much interest in the infrared and ultraviolet spectral characteristics of gaseous nitrogen oxyhalides such as nitrosyl (XNO), nitryl (XNO₂), nitrite (XONO), and nitrate (XONO₂, X = F, Cl, Br, or I) halides. Much of this interest has been associated with the chemical species containing F, Cl, and Br, since such compounds are thought to play an active role in the springtime depletion of ozone over Antarctica.^{1,2} In contrast, relatively little is known about the iodine-containing analogues. Although the iodine-containing compounds will probably be of little interest for stratrospheric chemistry, they could be of interest for an understanding of the iodine cycle in the troposphere, in particular iodine nitrate (IONO₂), which model simulations predict, along with hypoiodous acid (HOI), as one

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IR Spectra of Gaseous Nitrogen Oxyiodines

of the main gaseous reservoir species for iodine in the atmosphere, $^{3-5}$ is of interest.

The gaseous UV spectrum of nitrosyl iodine (INO) has been measured by a number of workers;⁶⁻⁸ however, to date only the infrared spectrum of this compound isolated in a krypton matrix has been published.^{9,10} An infrared spectrum of nitryl iodine (INO₂) isolated in an argon matrix has been reported¹¹ and unsuccessful attempts to record its gas-phase infrared spectrum have been made by Uthman et al.¹² No information could be found in the literature on iodine nitrite (IONO). Although iodine nitrate (IONO₂) has been synthesized in the laboratory¹³ neither its ultraviolet nor infrared spectrum has been reported in the literature.

We report here, for the first time, on the gas-phase FTIR spectra of the nitrogen oxyiodines INO, INO_2 , and $IONO_2$ obtained in I_2 -NO_x-N₂ photolysis mixtures. Some implications of the results for the atmospheric iodine cycle are discussed.

2. Experimental Section

The experiments were mostly performed in a 10.8-L Duran glass reaction chamber containing a White mirror system with a total path length of 44.8 m (1.5 m long, 28 passes) at 298 \pm 2 K. Analyses of reactants and products were made in situ using a Bruker IFS 88 Fourier-transform IR spectrometer equipped with a narrow-band Hg-Cd-Te detector. Some experiments were also performed in a 420-L Duran glass reactor also containing a White mirror system and equipped with a FTIR facility (Nicolet 7199) which has been described previously.¹⁴

The various compounds were generated in situ in the reaction chamber, as described in detail below, by irradiation of I_2 -NO or I_2 -NO₂ mixtures in 1013 mbar of N₂ using either Philips super actinic 40W/05 (320 < λ < 480 nm; λ_{max} = 365 nm) or Philips gold fluorescent lamps (TLD 36W/16; 500 < λ < 700 nm). The I_2 concentration was approximately 0.2 mbar and the concentrations of both NO and NO₂ were in the range 0.02-0.1 mbar.

Nitrosyl iodide (INO) was generated by the photolysis of I_2 using the gold fluorescent lamps in the presence of NO according to

 $I_2 + h\nu (500 < \lambda < 700 \text{ nm}) \rightarrow 2I$ $I + NO + M \leftrightarrow INO + M$

Nitryl iodide (INO_2) was produced by the photolysis of I₂ with the gold fluorescent lamps in the presence of NO₂ according to

$$l_2 + h\nu (500 < \lambda < 700 \text{ nm}) \rightarrow 21$$
$$I + NO_2 + M \leftrightarrow INO_2 + M$$

There is an alternative pathway for the reaction of I atoms with NO_2 . They can also add to the oxygen atom of NO_2 forming iodine nitrite (IONO):

$$I + NO_2 + M \leftrightarrow IONO + M$$

However, as will be discussed later, this pathway appears to be

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Figure 1. Residual spectrum after subtraction of NO and small amounts of NO₂, HNO₃, and H₂O impurities from the product spectrum obtained after 30-s irradiation with the gold fluorescent lamps of a NO-I₂-N₂ photolysis mixture.



Figure 2. Product spectrum of an I_2 -NO₂-N₂ photolysis mixture after 30-s irradiation with the gold fluorescent lamps. Contributions from NO, HONO, HNO₃, and H₂O have been subtracted.

TABLE I: Molecular Vibrational Frequencies of Nitrosyl Halogenides (XNO) $(cm^{-1})^a$

	a	ssignmen	t		
compd	(NO str)	$(bend)^{\nu_2}$	(NS str)	state	ref
FNO	1852	751	509	N ₂ matrix	15
	1844	767	521	gas	16
CINO	1806	585	322	Ar matrix	10, 17
	1800	596	332	gas	16, 18
BrNO	1801	536	259	Ar matrix	10
	1801	542	265	gas	16, 19, 20
INO	1809	470	216	Ar matrix	9, 10
	1785			gas	this work

^a Assignments and approximate descriptions of the modes are from ref 10.

of negligible importance under the present experimental conditions. Iodine nitrate (IONO₂) was generated by the photolysis of NO₂

using the super actinic lamps in the presence of I_2 according to

 $NO_2 + h\nu (320 < \lambda < 480 \text{ nm}) \rightarrow NO + O$

$$O + I_2 \rightarrow IO + I$$

 $IO + NO_2 + M \rightarrow IONO_2 + M$

The IR absorption spectra as a function of irradiation time were recorded at 1-cm^{-1} resolution by coadding 32 interferograms over a period of 15 s. Typical time-resolved data were obtained in the range 600-4000 cm⁻¹ by recording 6-12 spectra successively.

3. Results and Discussion

Figure 1 shows the product spectrum in the wavenumber range 750–2000 cm⁻¹ obtained after 30-s irradiation of a I_2 -NO-N₂ mixture using the gold fluorescent lamps in which contributions due to absorptions of NO and NO₂ impurity have been subtracted. A weak absorption with a band center at 1785 cm⁻¹ is clearly

TABLE II: Molecular Vibrational Frequencies of Nitryl Halogenides (XNO₂) (cm⁻¹)^a

	assignment							
compd	$(NO_2 \text{ sym str})$	$(NO_2^{\nu_2} sciss)$	$(NX^{\nu_3} str)$	(NO ₂ asym str)	$(NO_2^{\nu_5} wag)$	ν ₆ (opd)	state	ref
FNO ₂	1312.0	812.1	562.9	1802.9	557.7	737.9	N_2 matrix	15
-	1309.6	822.4	567.8	1791.5	559.6	742	gas	23-27
CINO,	1264.3	787.0	365.0	1674.8			Ār matrix	28
-	1267.1	792.6	369.6	1684.6	408.1	652.3	gas	23-26, 29
BrNO ₂	1288.9	784.0	496	1659.9	401.8	574.4	Ar matrix	11, 21, 23, 30
-	1292	787		1660			gas	31
INO ₂	1279	569	468	1700	305	650	Ar matrix	11, 21, 30
•	1282	778					gas	this work

^a Assignments and approximate descriptions of the modes are from refs 22 and 20.

visible. The region around 1785 cm⁻¹ is expanded in the inset in Figure 1. Absorptions at about 1800 cm⁻¹ are typical for NO stretching vibrations and the absorption observed in the present work is assigned to INO. It is compared with the absorptions of other nitrosyl halogenides in Table I. This represents the first report of the gas-phase IR spectrum of INO.

The value of 1785 cm⁻¹ obtained here as band center for INO is 25 cm⁻¹ lower than the value obtained from a IR spectrum of this molecule isolated in a krypton matrix.^{8,9} A look at Table I shows that, in general, the frequencies of the NO-stretching vibration for the gas phase nitrosyl halogenides are lower than those of the corresponding matrix isolated molecule. Further the value of 1785 cm⁻¹ fits in with the observed order of the NO stretching frequencies for the nitrosyl halogenides, i.e., I < Br < Cl < F.

Figure 2 shows the product spectrum of a I_2 -NO₂-N₂ reaction mixture after 30-s irradiation using the gold fluorescence lamps. Two absorptions of approximately equal intensity are observed with band centers at 1282.5 and 778 cm⁻¹ in which contributions from HNO₃ impurity formed from heterogenous reactions of NO₂ have been subtracted. On further irradiation of the mixture, the two bands diminish in intensity and weak absorptions are observed at 1263.8, 852.2, and 790.3 cm⁻¹. On switching off the fluorescent lamps the absorptions at 1282.5 and 778 cm⁻¹ rapidly disappear and the absorptions at 1263.8, 852.2, and 790.3 cm⁻¹ increase in intensity. The new absorptions are due to nitrous acid (HONO),²¹ which is probably being formed heterogeneously at the reactor walls.

As mentioned earlier there are two channels for the reaction of I atoms with NO₂, one leading to the formation of IONO and the other to the formation of INO2. In previous studies on the recombination of iodine atoms in the presence of NO2 it has been assumed that the pathway giving INO_2 dominates.²² From a comparison of the vibrational frequencies of other nitryl halogenides (Table II) the absorptions at 1282.5 and 778 cm⁻¹ are

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a) In - NOn - No photolysis mixture after 30 s irradiation



b) Residual spectrum after subtraction of N₂O₅



Figure 3. (a) Product spectra of an I_2 -NO₂-N₂ photolysis mixture after 30-s irradiation with the super actinic lamps and (b) residual spectrum after subtraction of N₂O₅ from spectrum a.

assigned to the NO_2 symmetric stretch and NO_2 deformation of INO_2 , respectively. The asymmetric stretching vibration of NO_2 would be expected to be in the region of 1650 cm⁻¹. However, because of the strong absorption of NO2, which saturates this region, it was not possible to observe this band.

Niki et al.³² have shown in an FTIR study of the reaction of Cl atoms with NO₂ that the Cl atom adds mainly to the O atom forming chlorine nitrite

$$Cl + NO_2 \rightarrow ClONO$$

which then isomerizes to nitryl chloride

$$Cl + NO_2 \rightarrow ClNO_2$$

which is thermochemically more stable. Halogen nitrites show strong absorptions at around 1700 cm⁻¹ from NO₂ asymmetric

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TABLE III: Molecular Vibrational Frequencies of Halogen Nitrates (XONO₂) and HONO₂ (cm⁻¹)^a

	assignment								
compd	(NO ₂ asym str)	(NO ₂ sym str)	(OX str)	$(NO_2 \text{ sciss})$	$(NO_2 rock)$	(NO str)	state	ref	
HONO ₂	1708	1325	3550	879	579	647	gas	33	
FONO ₂	1759.1	1300.9	927.7	803.7	630	454.5	gas	25, 34-36	
CIONO ₂	1726.9	1287.6	807.7	781.3	556.6	428.3	Ar matrix	36, 37	
-	1735.4	1291.9	809.3	780.2	560.0	434.1	gas	25, 26, 34, 38-44	
BrONO ₂	1702	1285	750	805	572	(398)	N_2 matrix	45	
-	1711	1285	(690)	802	560	(390)	gas	44, 45	
IONO ₂	1673	1276		815	(580)		gas	this work	

^a Assignments in point group C_i and approximate descriptions of the modes are from refs 24 and 44.

stretching vibrations,^{21,30} which are generally 40-60 cm⁻¹ higher than those of the corresponding vibrations of nitryl halogenides. In the present work no absorption could be seen in the region around 1700 cm⁻¹, even at very short irradiation times. For comparison purposes Cl₂-NO₂-N₂ and Br₂-NO₂-N₂ photolysis systems were also investigated. In the Cl₂-containing system the formation of CIONO followed by isomerization to CINO₂ was clearly evident, in agreement with the previous findings of Niki et al.³² In the Br₂-containing system, formation of a compound with band centers at 1292 and 787 cm⁻¹ was observed. These bands are in agreement with those reported by Finlayson-Pitts et al.³¹ for $BrNO_2$ formed via the reaction of N_2O_5 with Br_2 or BrNO. No evidence was found for the formation of BrONO. It would appear that either IONO and BrONO are very short lived and therefore not detectable on the time scale of our experiments or the reactions of I and Br atoms with NO₂ lead directly to the formation of the nitryl halogenide rather than the halogen nitrite. Other work in this laboratory in the 420-L reactor has shown that INO_2 is also formed in the photolysis of $CH_3I-NO_2-N_2$ reaction mixtures:

$$CH_{3}I + h\nu \rightarrow CH_{3} + I$$
$$I + NO_{2} \rightarrow INO_{2}$$

In these systems, which were relatively free from interfering absorptions in the 1700-cm⁻¹ region, there was once again no indication for the formation of IONO.

Figure 3a shows the product spectrum in the region 700-2000 cm^{-1} of an I₂-NO₂-N₂ reaction mixture after 30-s irradiation using the Philips fluorescent lamps in which contributions from HNO₃ have been subtracted. The absorptions at 1717, 1244, and 742 cm^{-1} are due to N₂O₅. Figure 3b shows the residual spectrum after the absorptions due to N_2O_5 have been subtracted in which three doublet peaks with band centers at 1673, 1276, and 813 cm⁻¹ can be seen. From a comparison of the absorption spectra of other halogen nitrates (Table III), the absorptions are assigned to the NO₂ asymmetric stretch, NO₂ symmetric stretch, and NO stretch, respectively, of iodine nitrate (IONO₂). Investigations in the 420-L reactor in which spectra could be recorded down to 450 cm⁻¹ showed the presence of a weak absorption at 580 cm⁻¹. This weak absorption is tentatively assigned to the O-I stretching vibration

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of IONO₂. Weak absorptions due to INO₂ were also observed at the side of the 1276-cm⁻¹ band. The formation of HNO₃ is attributed to the heterogeneous reaction of NO₂ and/or IONO₂ at the reactor walls. The IONO₂ is almost certainly being formed in the reaction system via the following reactions:

$$NO_2 + h\nu (320 < \lambda < 450 \text{ nm}) \rightarrow NO + O$$

$$O + I_2 \rightarrow IO + I$$

$$10 + NO_2 \rightarrow IONO_2$$

Recently, Christe et al.⁴⁶ reported the formation of a product in one of the fractions of the volatile products from KNO₃-IF₅ reactions whose infrared absorption spectrum exhibited bands at 1686, 1271, and 795 cm⁻¹. They tentatively assigned the bands to IONO₂ on the basis of a comparison with the absorption spectra of other halogen nitrates. The band positions are not in particularly good agreement with those determined in the present work. The present study has shown that gaseous IONO₂ is very short lived at room temperature and it is also known from synthesis of the pure compound¹³ that it begins to decompose above 5 °C. Christe et al.⁴⁶ do not give the conditions or the resolution under which their IR spectrum was recorded. However, on the basis of the low thermal stability of IONO₂ and the poor agreement of the band positions with the values reported here it seems probable that the substance observed by Christe et al.46 in their complex reaction system is some other nitrate-containing product.

It is unlikely that the N_2O_5 observed in the $I_2-NO_2-N_2$ photolysis mixture is being formed directly in the reaction system, it is more probable that NO₃ radicals are being directly produced, which with NO₂ rapidly establish the equilibrium

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$$

There are several possible formation channels for NO₃ radicals in the reaction system. The reaction of O atoms with NO_2 has two product channels; the major channel results in the formation of O_2 and NO_2 , while the other minor channel leads to the formation of NO₃ radicals:⁴⁷

$$O + NO_2 \rightarrow O_2 + NO (80\%, 298 \text{ K})$$

 $O + NO_2 + M \rightarrow NO_3 + M$ (20%, 298 K, 1 bar)

However, model simulations of the chemistry of the reaction system indicate that this pathway can only account for a small fraction of the N_2O_5 observed. The most probable route leading to the formation of NO₃ radicals and consequently N_2O_5 is the photolysis of IONO₂:

$$IONO_2 + h\nu \rightarrow NO_3 + I$$

Neither the spectral positions nor the cross sections of the absorptions are known in the ultraviolet for IONO₂, however, its spectrum is expected to be red-shifted and its absorption cross sections should be higher^{3,4} than those of ClONO₂ and BrONO₂.⁴⁸

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Preliminary investigations on the ultraviolet spectrum of $IONO_2$ in this laboratory indicate that this is indeed the case. Results from experiments in which both the intensity and wavelength of the photolysis light were varied strongly support the hypothesis that photolysis is the main source of NO_3 in the reaction system.

The reaction of Cl atoms with ClONO₂ is known to produce NO₃.⁴⁹ Although the heat of formation of IONO₂ is not known, it is expected to be greater than the value of $\Delta H^{\circ}_{f}(298)$ K) = 47 kJ mol⁻¹ reported for BrONO₂.⁴⁷ A value of 47 kJ mol⁻¹ or more would suffice to make the following reaction of I atoms with IONO₂ exothermic:

 $I + IONO_2 \rightarrow I_2 + NO_3,$ $(106.8) (\geq 47?) (72.8) (62.4)$

 $\Delta H(298 \text{ K}) = -18.6 \text{ kJ mol}^{-1}$

This reaction represents another possible source of NO_3 .

As mentioned above, IONO₂ has a very short lifetime in the reactor; it decayed in the dark with a first-order rate coefficient of $\sim 3.2 \times 10^{-2} \text{ s}^{-1}$ at 298 K. It is not clear at present whether this decay is due entirely to thermal loss or if other processes are involved. Heterogeneous losses can largely be discounted, since losses of this nature in the reactor generally occur at rates of $\sim 10^{-4} \text{ s}^{-1}$. The decay rate for IONO₂ is considerably higher than that which has been used in models of atmospheric iodine chemistry.⁴ The models predict that IONO₂ is an important reservoir species in the atmosphere. However, if the thermal lifetime of IONO₂ is as short as the experiments suggest then it would considerably reduce the importance of IONO₂ as an atmospheric reservoir for iodine. Possible effects may, however, be somewhat compensated by the result of a recent investigation of the kinetics for the reaction

(49) Wayne, R.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgat, G.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. Atmos. Environ. **1991**, 25A, 1. of IO with NO₂ to form $IONO_2^{50}$ which suggest that the rate coefficient is a factor 2 faster than previously thought.^{47,51} More kinetic studies on the thermal stability of $IONO_2$ and the reaction of IO with NO₂ are needed to resolve this problem.

Irrespective of the production route of N_2O_5 in the system it represents a potential continuous NO_3 radical source. Such a source could, for example, be used in relative kinetic determinations of rate coefficients for the reactions of NO_3 with hydrocarbons. The I atoms are virtually unreactive toward most hydrocarbons and the I₂/hydrocarbon ratio can be kept so large that O(³P) reactions with the hydrocarbons are virtually negligible. The feasibility of using I₂- NO_2 - N_2 gas mixtures as a continuous photolytic source of NO_3 radicals is currently being developed in this laboratory and first results are encouraging.

4. Conclusions

Gaseous infrared spectra are reported for INO, INO_2 , and $IONO_2$, whereby this study represents the very first report of a spectrum for $IONO_2$. Model simulations of the atmospheric iodine cycle indicate that $IONO_2$ should be an important reservoir species for iodine. However, the thermal stability of $IONO_2$ observed in the present study suggests that it may not be as important an atmospheric reservoir for iodine as previously predicted by the models.

The photolysis of $IONO_2$ appears to result in the formation of I atoms and NO_3 radicals. The photolysis of $IONO_2$ has potential for being applied as a continuous source of NO_3 radicals for use in laboratory studies of NO_3 reactions.

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Simulation of Raman Spectra of Formic Acid Monomer and Dimer in the Gaseous State by an Extended Molecular Mechanics Method

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Raman spectral simulation of the equilibrium mixtures of the dimer and the monomer of four isotopic formic acids in the gaseous state at room temperature has been carried out by using Raman intensity parameters estimated empirically on the basis of the bond polarizability model. The relative intensities of the fundamentals except for the OH stretching mode of the dimer, the isotope frequency shifts, and the depolarization ratios are well reproduced. The assignment of a strong Raman band of formic acid at 230 cm⁻¹ to the intermonomer O—H···O out-of-plane bending mode due to Bertie et al. was supported by its large intensity in this simulation. An incompatibility has been revealed between the spectroscopic and the thermodynamic data on the monomer–dimer equilibrium in the literature.

Introduction

The molecular mechanics calculation of the energies and the structures of polyatomic molecules can be extended to the simulation of their vibrational spectra by supplementing the empirical molecular model with suitable intensity parameters.¹ In a previous paper,² we reported the molecular mechanics simulation of the

thermodynamic quantities, the geometries, the vibrational frequencies, and the infrared absorption intensities of formic acid monomer and dimer. The charge flux through the OH bond of the dimer on its own stretching, $\partial q_{OH}/\partial r_{OH}$, was found to explain the large frequency shift as well as the intensification of the OH stretching band on the formation of the hydrogen bonds. The large splitting between the A_g and the B_u carbonyl stretching frequencies of the dimer and the extension of the carbonyl bond on the dimerization were successfully reproduced by introducing two charge fluxes with respect to the C=O stretching, $\partial q_{O=C}/\partial r_{C=O}$ and $\partial q_{O=H}/\partial r_{C=O}$. Furthermore, the OH stretching charge flux and the two C=O stretching charge fluxes in the dimer contribute

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