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Observation of the v_1 OH(OD) stretch of HOI and DOI by Fourier transform infrared emission spectroscopy

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The spectra of vibrationally hot HOI formed in the reaction of alkyl iodides with oxygen atoms are observed by Fourier transform infrared emission spectroscopy. The v = 1-3 levels of the OH stretch are observed via the $\Delta v = -1$ and $\Delta v = -2$ sequence bands. The spectrum of DOI is observed by using 2,2,2-d₃-iodoethane as the precursor in the oxygen atom reaction. The v = 1-4 levels of the OD stretch are observed in the $\Delta v = -1$ sequence band, and the v = 1-5 levels of the OD stretch are observed in $\Delta v = -2$. Medium resolution spectra (0.031 cm⁻¹ apodized) are recorded and rotationally analyzed for the ν_1 fundamental and $2\nu_1 - \nu_1$ hot band of HOI. An estimate of the HOI ground state structure is made by constraining the OH bond length to its value for HOCl and HOBr and calculating the HOI bond angle and the OI bond length by least squares fit to the ground state rotational constants. © 1996 American Institute of Physics. [S0021-9606(96)02418-6]

I. INTRODUCTION

The hypohalous acids belong to the series HOX, where X may be F, Cl, Br, or I. These are important atmospheric species, particularly HOCl and HOBr, since they are involved as intermediates in the catalytic destruction of ozone.1-10 Because of their importance in atmospheric chemistry and also because of their intrinsic, fundamental significance, much work is available on the gas phase spectroscopy of the first three acids in this series, HOF (Refs. 11-16), HOCl (Refs. 17-28), and HOBr (Refs. 29-31) in both the microwave and infrared regions. The number of investigations of the final member of this series, HOI, is far fewer, although it too is regarded as an important species in the chemistry of atmospheric iodine.^{32–35} Previous studies of HOI include the characterization of the UV-VIS absorption spectrum in the aqueous phase,^{36–37} and identification of the IR absorption spectrum of HOI and its isotopic variants in N₂ and Ar matrices.^{38–39} The first gas phase spectrum of HOI was reported by Barnes *et al.*⁴⁰ They observed the ν_1 OH stretch and the ν_2 bend mode at a resolution of 1 cm⁻¹.

The paucity of investigations of HOI perhaps lies in the difficulty of its synthesis. HOI has been speculated as a product in the radical-radical reaction between HO₂ and IO (Refs. 34 and 35) and also in the reaction of OH radical with iodine containing compounds (Refs. 41-44). Barnes et al.⁴⁰ made HOI by the reaction of OH radical with I₂, CH₃I, and CH₂I₂. The yield of HOI from these reactions is quite small. With a pathlength of 492 m they observed only a \sim 5% HOI absorption. We recently found the reaction between alkyl iodides and $O({}^{3}P)$ to be an effective method of synthesizing HOI.⁴⁵ Furthermore, the HOI produced in this reaction is found to be vibrationally very hot in the OH stretch, fluorescing strongly in the mid IR. We use the emission from hot HOI itself as the radiation source for the FTIR spectrometer. By directly measuring the HOI fluorescence, we are able to utilize a simple experimental arrangement and also exploit the inherently greater sensitivity of emission spectroscopy.⁴⁶ In forthcoming papers, we explore the mechanism of HOI formation in alkyl iodide+ $O({}^{3}P)$ reactions and analyze the nascent vibrational distribution of HOI produced in pulsed, time-resolved experiments,⁴⁷ and in a closely related paper, we report on the OH vibrational distribution produced in the reaction of alkyl radicals with $O({}^{3}P).{}^{47}$

In the following sections the fluorescence collection, Fourier transform infrared (FTIR) spectrometer, and data collection systems are described, as are the experimental details for producing HOI. Results are presented for the vibrational analysis of the OH and OD stretches of HOI and DOI. Rotation and distortion constants for the vibrational ground state, $v_1=1$ and $v_1=2$ of HOI are determined by combination-differences formed from the v_1 fundamental and $2\nu_1 - \nu_1$ hotband.

II. EXPERIMENTAL DETAILS

Vibrationally hot HOI is observed as a product in the reactions of oxygen atoms with iodoethane (C_2H_5I) , 1-iodopropane $(n-C_3H_7I)$, and 2-iodopropane $(i-C_3H_7I)$, the result of a novel, five-membered ring transition state:⁴⁵

$$\begin{split} & \mathrm{C_2H_5I+O(^3P)} \rightarrow \mathrm{HOI+C_2H_4}, \ \Delta_r H = -237 \ \mathrm{kJ/mol}, \\ & n\mathrm{-C_3H_7I+O(^3P)} \rightarrow \mathrm{HOI+C_3H_6}, \ \Delta_r H = -245 \ \mathrm{kJ/mol}, \\ & i\mathrm{-C_3H_7I+O(^3P)} \rightarrow \mathrm{HOI+C_3H_6}, \ \Delta_r H = -236 \ \mathrm{kJ/mol}. \end{split}$$

Grice and co-workers have also recently observed HOI formation in molecular beam scattering experiments between $O(^{3}P)$ and iodoethane.⁴⁸

The HOI product is only formed for alkyl chains of two carbon length or greater. Similar OH stretch vibrational distributions of the HOI product are observed for all three alkyl iodide precursors. Emission from $v_1=3$ is observed in both the $\Delta v = -1$ and $\Delta v = -2$ bands. This state has an energy of 10 374 cm⁻¹ which corresponds to \sim 50% of the available reaction exothermicity. 2-iodopropane is the precursor used for the HOI spectroscopic measurements presented here. The precursor for DOI is $2, 2, 2, -d_3$ -iodoethane.



FIG. 1. Low resolution (1 cm^{-1}) HOI emission spectrum with blackbody background subtracted and intensities normalized to the instrument response function. Emission is observed only for the OH stretch mode. Three quanta of OH stretch are observed in both the $\Delta v = -1$ and $\Delta v = -2$ sequence bands. The absorption feature at 2350 cm⁻¹ is due to atmospheric CO₂.

Continuous HOI emission is produced with a flow tube reactor. This consists of concentric quartz tubes, the outer 1.27 cm in diameter, the inner, 0.64 cm. The inner tube enters the outer tube approximately 1 cm from its outlet. Oxygen atoms are made by microwave discharge (2.45 GHz, ~90 W) in neat O₂ (99.998%) in the outer tube of the reactor. The backing pressure of O₂ in the discharge is ~500 Pa. The discharge is generated within an Evenson type cavity located 15 cm before the outlet of the reactor. At the outlet of the reactor, oxygen atoms formed in the discharge react with 2-iodoethane, which is fed through the inner concentric tube at a backing pressure of ~300 Pa.

The quartz tube reactor is placed within a larger stainless steel vacuum chamber containing Welsh cell fluorescence collection optics which couple the emission into the FTIR spectrometer. This chamber is evacuated by a blower pump, however, the cross section of the vacuum line exiting the chamber is reduced by a 2.5 cm diameter aperture in order to throttle down the pumping speed and increase the residence time of the hot HOI products in the observation region.

Infrared emission is collected by a Welsh cell^{49–50} in the main chamber and is f/number-matched by a telescope $(f_1=150 \text{ mm}, f_2=150 \text{ mm}, \text{CaF}_2)$ to the FTIR spectrometer. The modulated IR fluorescence signal is detected by a 77 K InSb detector, amplified with current and voltage amplifiers and sent to a homebuilt data acquisition system based on a commercial 16-bit A/D card in a PC and original software.

Three sets of emission spectra were recorded, one low resolution scan for both HOI and DOI and a higher resolution scan for HOI. We were not able to make a high resolution scan for DOI due to the limited quantity of the deuterated compound. The low resolution scans are 500 coadditions each recorded at 1 cm⁻¹ resolution and are shown in Figs. 1–3. The higher resolution scan for HOI, shown in Figs. 4–6, is 970 coadditions. Triangular apodization was used resulting in an apodized resolution of 0.031 cm⁻¹. The frequency range recorded was only limited by the



FIG. 2. Low resolution (1 cm^{-1}) DOI emission spectrum with blackbody background subtracted and intensities normalized to the instrument response function. Emission is observed only for the OD stretch mode. Four quanta of OD stretch are observed in the $\Delta v = -1$ sequence band. In the $\Delta v = -2$ sequence band $v_1 \leq 5$ is observed. A small amount of HOI emission is observed for the v_1 fundamental at 3625 cm⁻¹. This can be attributed to some minor contamination in the $2,2,2-d_3$ -iodoethane sample of other ethyl iodide isotopes which are only partially deuterated at the beta-carbon.

spectral responsivity of the InSb detector. Two times oversampling was used on all spectra. A commercial software package was used to calculate the Fourier transforms. To transform the higher resolution interferogram it was necessary to break it up, by taking every third point from its original 1.48 million points, into three interferograms of 494 660 points each. Each of these spectra were separately transformed with a Nyquist frequency set to 5266.0033 cm⁻¹, and the resulting spectra were coadded. No emission from the HOI overtones was observed within the signal-to-noise ratio of the higher resolution spectrum, so spectral folding problems were not encountered by this operation. Each interferogram was corrected in phase from a small part of the interferogram itself.



FIG. 3. Expanded portion of low resolution (1 cm^{-1}) HOI spectrum showing the ν_1 fundamental, 3625 cm⁻¹ and the $2\nu_1 - \nu_1$ hotband, 3458 cm⁻¹. The *b*-type band *Q* branches for the fundamental are clearly evident and are labeled in symmetric top notation.



FIG. 4. A portion of the high resolution (0.031 cm⁻¹ apodized) HOI spectrum showing the ${}^{Q}R$ branch of the ν_1 fundamental with rotational assignments indicated. Many of the transitions for the different K_a subbands overlap each other, although for each K_a there is some value of J at which the transition is not blended. Resolved $K_a=1$ asymmetry doublets are indicated by the Wang symmetry parameter γ .

OH emission, which likely comes from the reaction sequence

i-C₃H₇I+O(³P) \rightarrow IO+i-C₃H₇•, $\Delta_r H = 9$ kJ/mol C₃H₇•+O(³P) \rightarrow OH+C₃H₆, $\Delta_r H = -283$ kJ/mol,

is observed in the higher resolution HOI spectrum. These radical-radical reactions are investigated in more detail by pulsed laser photolysis experiments.⁴⁷ The OH emission allows a convenient check to the calibration of the interferogram with respect to the reference HeNe laser of the FTIR. Twenty-two OH emission lines were observed over the frequency range 3330–3680 cm⁻¹. Comparison of observed OH line positions to those reported in the literature^{51–52} shows randomly distributed deviations of less than ± 0.004 cm⁻¹. The observed spectra are not recalibrated.



FIG. 5. The $\nu_1^{P}P_3$ branch of HOI taken from the high resolution (0.031 cm⁻¹ apodized) spectrum. The transitions indicated here are the only individual rovibrational transitions of the perpendicular *b*-type band from the high resolution spectrum which could be observed in the spectrum. The two transitions marked with an asterisk are OH emission lines which were among those used as an internal calibration reference.



FIG. 6. A portion of the high resolution (0.031 cm⁻¹ apodized) HOI spectrum showing the ${}^{Q}R$ branch of the $2\nu_1 - \nu_1$ hotband with rotational assignments indicated. Resolved $K_a = 1$ asymmetry doublets are indicated by the Wang symmetry parameter γ . The transition marked with an asterisk is an OH emission line which was used as an internal check on the frequency calibration.

III. DESCRIPTION OF THE SPECTRA AND ASSIGNMENTS

Figures 1 and 2 show the low resolution (1 cm^{-1}) HOI and DOI emission spectra obtained from the alkyl iodide+O reactions. The intensity of these emission spectra are normalized by first subtracting out the background, room temperature blackbody spectrum, and dividing the result by the instrument response function of the FTIR optics and the InSb detector. The instrument response function is determined from the observed emission of a calibrated blackbody source compared with the theoretical emission of an ideal blackbody. In both spectra the only vibrational bands observed belong to the $\Delta v = -1$ and $\Delta v = -2$ sequence bands of the OH(OD) stretch. In the HOI spectrum, Fig. 1, emission is observed in both sequence bands for $v \leq 3$. In the DOI spectrum, Fig. 2, emission from $v \leq 5$ is observed in the $\Delta v = -2$ sequence band, and for $v \leq 4$ for the $\Delta v = -1$ sequence band.

An expanded portion of the HOI low resolution spectrum is shown in Fig. 3. Prominent in Fig. 3 are the ν_1 fundamental at 3626 cm⁻¹ and the $2\nu_1 - \nu_1$ hot band at 3459 cm⁻¹. As is the case for the ν_1 fundamentals of HOF (Ref. 16), HOCl (Refs. 18 and 26), and HOBr (Ref. 31) the ν_1 of HOI is a hybrid band consisting of both *a*-type and *b*-type transitions. HOI is an accidental, prolate symmetric top, $\kappa = -0.9996$, and except for the $K_a = 1$ subbands, where asymmetry doubling is observed, its transitions are those of a prolate symmetric top. The Q bandheads of the perpendicular b-type band are very obvious in Fig. 3. The A constant for HOI is greater than 20 cm⁻¹, so these Q bandheads spread over $\sim 500 \text{ cm}^{-1}$ and are immediately assignable by inspection. They are labeled in Fig. 3 using symmetric top notation. The parallel *a*-type transitions of the fundamental are much more congested and lie near the band center. They are not resolved in the low resolution spectrum of Fig. 3, however, in the higher resolution spectrum individual rotational lines in the parallel band are resolved. A small portion of the ${}^{Q}R$ branch of the fundamental is shown in Fig. 4 along with lines indicating the rotational assignments. At our apodized resolution of 0.031 cm⁻¹, many rotational lines of the different K_a subbands are overlapped.

The majority of assignable lines in the v_1 band belong to the parallel type transition. However, it is fortunate that ν_1 is a hybrid band, since without the perpendicular type transitions it would be possible to obtain only the difference in the rotational A constants for the upper and ground states, not their absolute values. Fitting of the spectrum began with the ${}^{P}Q$ and ${}^{R}Q$ bandheads of the perpendicular transition. These alone quite well define the band center and A rotational constants in the ground state and in ν_1 . A reasonable initial estimate of the B and C rotational constants is obtained by setting them to one half the spacing between the strong $K_a=2$ transitions evident in Fig. 4. Fitting proceeds smoothly by simulating a stick spectrum, making new assignments, including them in the fit, and simulating a new stick spectrum. A criterion for the correct assignment is that the new fit predicts additional lines of the band not included in the previous fit.

While the ${}^{P}Q$ and ${}^{R}Q$ bandheads are strong, no individual rotational lines of the perpendicular band were observed within the signal-to-noise of the spectrum with the exception of the ^PP $K_a=3$ subband. Here individual rotational transitions with J''=3-30 are assignable. This portion of the spectrum is displayed in Fig. 5.

The $2\nu_1 - \nu_1$ hot band is also a hybrid having both *a*-type and *b*-type transitions. From the low resolution spectrum it is possible to identify ${}^{P}Q$ bandheads of the *b*-type perpendicular band having $K_a \leq 6$. The ^{*R*}*Q* bandheads having $K_a > 2$ are difficult to identify as they overlap with the congested *a*-type parallel transitions of the ν_1 fundamental. From the higher resolution HOI spectrum it is also possible to identify and assign lines belonging to the *a*-type band of $2\nu_1 - \nu_1$. A portion of the ${}^{Q}R$ branch of the parallel band is shown in Fig. 6 along with the rotational assignments.

IV. VIBRATIONAL ANALYSIS

The band centers of the vibrational transitions for the $\Delta v = -1$ and $\Delta v = -2$ sequence bands observed in the low resolution spectra of HOI and DOI are listed in Table I. The band center frequencies are taken as the minimum between the ${}^{Q}P$ and ${}^{Q}R$ branch contours of the lower resolution spectra. This is a crude estimate of the band center and is assigned an appropriate error of $\pm 5 \text{ cm}^{-1}$. These vibrational transitions, which are only observed for the OH(OD) stretch, are fit to the vibrational term value expression for a polyatomic, anharmonic oscillator,⁵³ Eq. (1).

$$G_{v_1 v_2 v_3} = \sum_r \omega_r (v_r + \frac{1}{2}) + \sum_{r \leqslant s} x_{rs} (v_r + \frac{1}{2}) (v_s + \frac{1}{2}) + \cdots$$
 (1)

Terms involving v_2 and v_3 , which are always zero in this case, cancel out, leaving a simplified expression, Eq. (2), for the vibrational transitions observed for the OH(OD) stretch,

TABLE I. Band centers and vibrational parameters (in cm⁻¹) for HOI and DOI $\Delta v_1 = -1$ and $\Delta v_1 = -2$ sequence bands. Band centers are taken from the 1 cm⁻¹ spectra as the minimum between the ^{Q}P and ^{Q}R branches. Their errors are $\pm 5 \text{ cm}^{-1}$.

	HOI	DOI			
	$\Delta v_1 = -1$				
1-0	3625 ^a	2674			
2-1	3458 ^a	2585			
3-2	3292	2498			
4-3		2409			
	$\Delta v_1 = -2$				
2-0	7081 ^a	5258			
3-1	6751	5084			
4-2		4910			
5-3		4739			
Vibrational Parameters					
$\left(\omega_1 + \frac{x_{12}}{2} + \frac{x_{13}}{2}\right)$	3789.37(40)	2759.35(38)			
x ₁₁	-82.825(97)	-43.445(61)			

^aSee Table III for band centers determined from fit to rotationally resolved spectra.

$$G_{v_1}' - G_{v_1}'' = \left(\omega_1 + \frac{x_{12}}{2} + \frac{x_{13}}{2}\right) (v_1' + \frac{1}{2}) + x_{11}(v_1' + \frac{1}{2})^2 - \left(\omega_1 + \frac{x_{12}}{2} + \frac{x_{13}}{2}\right) (v_1'' + \frac{1}{2}) - x_{11}(v_1'' + \frac{1}{2})^2.$$
(2)

From a fit of Eq. (2) to the observed transitions, the vibrational anharmonicity constant, x_{11} , for the OH(OD) stretch is determined. For HOI we obtain $x_{11} = -82.825(97)$ cm^{-1} , and for DOI, $-43.445(61) cm^{-1}$. Because we observe only transitions which involve the OH(OD) stretch, the vibrational equilibrium frequency, ω_1 , cannot be determined independent of the cross anharmonicity terms x_{12} and x_{13} .

The anharmonicities for the OH(OD) stretches of HOF(DOF) (Refs. 54 and 55), HOCl(DOCl) (Ref. 56), and OH(OD) (Ref. 57) radical are also known. x_{11} for HOI and DOI is very similar to that found for hydroxyl (-84.881) cm^{-1}) and deuterated hydroxyl (-44.055 cm^{-1}) radicals, and also to that for HOF (-85.24 cm^{-1}) and DOF (-45.14 cm^{-1}) cm^{-1}). The x_{11} anharmonicities for HOCl and DOCl, -97.50 cm⁻¹ and -51.72 cm⁻¹, respectively, are $\sim 15\%$ higher.

V. RO-VIBRATIONAL ANALYSIS

Because this is the first investigation of the rotational structure of HOI, there are no highly accurate microwave data to assist in determining the ground state constants of this molecule. To avoid any difficulties which might arise from correlations in lower and upper state rotational constants when both sets are simultaneously determined by fitting transition frequencies, and also to produce error estimates which more accurately reflect the quality of the data, we use the technique of combination differences to determine the rotation and distortion constants for the ground state, $\nu_1 = 1$, and $\nu_1 = 2$ levels. In determining the rotational constants for $\nu_1 = 1$, combination differences can be made

TABLE II. Range of J" and K_a'' for observed transitions in HOI ν_1 fundamental and $2\nu_1 - \nu_1$ hotband.

Single Ro-vibrational transitions	ν_1 Fundamental J'' range	$2\nu_1 - \nu_1$ hotband J'' range
$^{Q}P_{0}$	2-45	4-15, 17-34
${}^{Q}P_{1}\gamma^{a}=0$	14-27, 29-38	4-14, 16-29
$^{Q}P_{1}\gamma^{a}=1$	14-18, 21-38	4-8, 10-14, 16-29
Q_{P_2}	3-4, 6-45	4-36
Q_{P_3}	4-38	4-24
Q_{R_0}	2-40	4–29
${}^{Q}R_{1}\gamma^{a}=0$	10-37	6-22, 24-30
$QR_1 \gamma^a = 1$	10-37	6-8, 10-30
Q_{R_2}	3-40	8-15, 17-27, 29-35
Q_{R_3}	4-28, 30-32	17-35
$^{P}P_{3}$	3-30	
Q bandhead	ν_1 Fundamental	$2\nu_1 - \nu_1$ hotband
transitions	K''_a range	K''_a range
^P O	1–7	1-6
$R\tilde{Q}$	0-5	0
~		

^aWang asymmetry parameter.

from transitions involving both the v_1 fundamental and the $2\nu_1 - \nu_1$ hotband. Due to the better signal-to-noise ratio for the spectrum of the v_1 fundamental only these transitions are used for determining the ν_1 rotation and distortion constants. The transitions used in forming combination differences are taken from both the low and higher resolution spectra. The range of J and K_a quantum numbers observed for the v_1 fundamental, and also the $2\nu_1 - \nu_1$ hot band, are listed in Table II.

In the higher resolution HOI spectrum, 370 transitions are assigned in the ν_1 fundamental. Of these, approximately one third are blended lines. Blended lines are given a greater uncertainty than unblended lines in the fitting procedure. A ro-vibrational line assigned to only one transition is given an uncertainty of 0.01 cm⁻¹. Lines which can be assigned to two transitions are given an uncertainty of 0.02 cm^{-1} , and lines which can be assigned to more than two transitions are omitted from the fit. The same criteria for assigning uncertainties are applied to transitions in the $2\nu_1 - \nu_1$ hotband.

Of the 370 transitions taken from the higher resolution HOI spectrum for the ν_1 fundamental, only 28 belong to the perpendicular transition. These are all from the ${}^{P}P K_{a}=3$ subband. To obtain the A rotational constants with greater accuracy it is necessary to include more $\Delta K_a = \pm 1$ transitions from the perpendicular band. The perpendicular ${}^{R}Q$ and ${}^{P}Q$ bandheads are easily identified from the low resolution spectrum. Thirteen of these bandheads for $K_a \leq 7$ are included in the fit and are given an appropriately greater uncertainty of ± 0.5 cm⁻¹. The perpendicular Q bandheads are a convolution of all the overlapping $\Delta J = 0$ transitions having $\Delta K_a = \pm 1$. In the fit, the Q bandheads are treated as a single transition assigned a median J value, J=15.

The rotational analysis of HOI is based on the Hamiltonian of a near prolate asymmetric rotor, type \mathbf{I}^r representation. The symmetric top reduction (S) of the molecular Hamiltonian is used.⁵⁸ Centrifugal distortion terms up to the 7407

fourth order are included. The rotational wave functions are expanded in terms of a symmetric rotor basis set. The Hamiltonian is taken from Eqs. (8.110)-(8.112) of Ref. 58. The diagonal and off-diagonal matrix elements as used in the fitting procedure are given in

$$\langle v, J, k_a | \mathbf{H} | v, J, k_a \rangle = \nu_0 + \frac{1}{2} (B_v + C_v) [J(J+1) - k_a^2] + A_v k_a^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1) k_a^2 - D_K k_a^4,$$
(3)
$$\langle v, J, k_a | \mathbf{H} | v, J, k_a \pm 2 \rangle = \frac{1}{4} (B_v - C_v) [f_{\pm}(0) f_{\pm}(1)]^{1/2}$$

$$-d_1J(J+1)[f_+(0)f_+(1)]^{1/2},$$
 (4)

$$\langle v, J, k_a | \mathbf{H} | v, J, k_a \pm 4 \rangle = d_2 [f_{\pm}(0) f_{\pm}(1) f_{\pm}(2) f_{\pm}(3)]^{1/2},$$
(5)

$$f_{\pm}(l) = [J(J+1) - (k_a \pm l)(k_a \pm l \pm 1)].$$
(6)

In Eqs. (3)–(6), v and J are the vibrational and total angular momentum quantum numbers. The pseudo-quantum number k_a corresponds to the signed value of K in the symmetric rotor basis. A_v , B_v , and C_v are the effective rotational constants, and D_J , D_{JK} , D_K , d_1 , and d_2 are the quartic centrifugal distortion constants of the symmetric top reduced Hamiltonian.

For each J the Hamiltonian matrix is written in the symmetric top basis and is subjected to a Wang transformation.⁵⁸ The resulting four Wang submatrices are diagonalized independently. Only for the $K_a = 1$ subbands is the asymmetry doubling observed. For all other K_a subbands the splitting between the asymmetry doublets is less than the instrumental resolution. For example, the calculated splitting at ${}^{Q}R_{2}(30)$ is only 0.006 cm⁻¹. For all $K_a > 1$ subbands where asymmetry doubling is not observable, the term values are taken as the mean of those calculated for the symmetric, $\gamma=0$, and antisymmetric, $\gamma = 1$, Wang functions.

The rotation and distortion constants for the ground state and $\nu_1 = 1$ of HOI are determined from fitting the Hamiltonian given above to combination differences of the ν_1 fundamental. The rotation constants for $\nu_1=2$ are determined from combination differences of the $2\nu_1 - \nu_1$ hotband. From the 370 transitions observed for the ν_1 fundamental, 226 combination difference pairs are derived for the ground state and 223 for $\nu_1=1$. For $\nu_1=2$, there are 109 combination differences derived from 259 assigned transitions in the $2\nu_1 - \nu_1$ hotband. Each combination difference is given an uncertainty equal to the square root of the sum of squares of the uncertainties for the transitions from which it is made. The four Wang submatrices are diagonalized numerically, and computed combination differences are least squares fit to the measured values. Iteration of fit parameters is continued until the reduced chi-squared varies by less than 0.001. The d_2 off-diagonal centrifugal distortion term is found to be not statistically significant with this data set and is therefore constrained to zero. Likewise, inclusion of centrifugal distortion terms higher than fourth order did not significantly improve the quality of the fit. The centrifugal distortion terms for $v_1=2$ are not well determined from the combination differ-

TABLE III. Spectroscopic constants determined by combination differences for HOI ground state, $v_1=1$, and $v_1 = 2$ (in cm⁻¹), S Reduction; I' representation.

	Ground state	<i>v</i> ₁ =1	<i>v</i> ₁ =2
ν_0		3625.84(1) ^a	7084.74(5) ^a
A	20.934 75(109) ^b	20.079 60(235)	19.257 2(237)
В	0.278 939 8(285)	0.278 457 1(337)	0.277 992 3(226)
С	0.275 070 8(271)	0.274 461 0(326)	0.273 946 8(209)
$D_{J} \times 10^{6}$	0.235 76(314)	0.236 09(375)	0.236 09 ^c
$D_{JK} \times 10^6$	20.032(306)	19.536(405)	19.536 ^c
$D_K \times 10^3$	5.727 6(824)	5.508(180)	5.508 ^c
$d_1 \times 10^9$	-18.54(648)	-23.03(768)	-23.03 ^c
d_2^{d}	0.0	0.0	0.0
No. of comb. diff.	226	223	109
$\chi^{2 e}_{\nu}$	0.25	0.32	0.66

^aBand origins are determined in a separate fit to transition frequencies constraining rotational constants to values determined by combination differences. The number in parentheses is an estimate of the uncertainty for the band center.

^bOne standard deviation in parentheses.

 $v_1=2$ distortion constants are constrained to the values determined for $v_1=1$.

^dThe d_2 term is constrained to zero.

 ${}^{e}\chi^{2}_{\nu} = \chi^{2}/\nu$, where ν is the number of observations less the degrees of freedom.

ences of the $2\nu_1 - \nu_1$ hotband alone. In the final fit, these terms are constrained to the values determined for $v_1 = 1$ and only the A, B, and C rotational constants for $v_1=2$ are allowed to vary. The constants derived for these three states are listed in Table III.

The band centers for ν_1 and $2\nu_1$ cannot be determined by combination differences. In order to obtain these constants, transition frequencies are fit instead of combination differences. Two techniques are used. In the first, the lower and upper state constants are fixed to those determined by combination differences and only the band center for the upper state is treated as an adjustable parameter. In the second technique, only the lower state constants are fixed to those determined by combination differences while all rotation and distortion constants for the upper state are allowed to float in the fit. The difference in the band centers determined by the two techniques is used as an estimate in the error for the band center. In addition to determining the band center, fitting the transitions also provides a consistency check on the constants determined by combination differences. The rotation and distortion constants determined by fitting transitions are the same as those determined in the combination difference fit within the more conservative confidence interval for the combination difference fit.

Calculation of the inertial defect for HOI in its ground vibrational state is also a valuable tool in checking the validity of the rotational constants. The inertial defect, Eq. 7, is the difference between the largest moment of inertia, that about the c axis, and the sum of the moments of inertia about the *a* and *b* axes:

$$I_{c}^{\nu} - (I_{b}^{\nu} + I_{a}^{\nu}) = \Delta_{\nu}.$$
⁽⁷⁾

For planar rigid rotors the inertial defect is zero, and any one of the moments of inertia is determined by the other two. However, vibrational effects cause the inertial defect to be nonzero in real molecules, although for a necessarily planar molecule such as HOI the deviation is expected to be small. The inertial defect for the ground vibrational state of HOI is indeed small. From the inverse of the rotational constants in Table III, the calculated inertial defect for the ground vibrational state of HOI is 0.0026(5) cm or 0.045(8) amu Å². The ground state inertial defect for HOI is similar in magnitude and sign to those determined for HOCl (Ref. 24), 0.0642(1) amu Å², and HOBr (Ref. 31), 0.067 175(16) amu Å².

VI. DISCUSSION

With the work presented here, rotationally resolved spectroscopic observations have been made of all the hypohalous acids. In Table IV the ground state constants and molecular structures which have been determined for this series are summarized. In the current work no rotational constants for the isotopically substituted species DOI were determined, so the structure of HOI can not be evaluated directly. However, the consistency of the ground state rotational constants found for HOI can be compared with known structures of the other molecules in this series by constraining one of the molecular parameters. In their recent work on the v_1 fundamental of HOBr, Cohen *et al.*³¹ noted that the OH bond length is nearly the same in HOCl and HOBr. They constrained the OH bond length in HOBr to that determined for HOCl and calculated the corresponding bond angle and OBr bond length by best least squares fit to their rotational constants. In a similar manner we also constrain the OH bond length in HOI to 0.9643 Å (the value determined for HOCl and used by Cohen et al.³¹ for HOBr) and calculate the HOI bond angle and OI bond length from a least squares fit to the three ground state rotational constants; these are reported in Table IV. Although the molecular parameters determined in this way for HOI have large uncertainties, the values are quite consistent with those known for the other hypohalous acids. Ruscic and Berkowitz⁵⁹ have compared the OX bond length in HOX to that of the diatomic molecule and noted that the ratio is nearly constant in

HC35Clb HO⁷⁹Br^c HOF HOId 19.534 564 20.470 159 A_{0} 20.463 616 20.935 B_0 0.892 724 1 0.504 241 82 0.352 797 66 0.278 94 0.850 833 4 0.491 199 20 0.346 341 65 0.275 07 C_0 $D_J \times 10^6$ 0.897 19 0.429 5 3.1768 0.236 $D_{JK} \times 10^6$ 80.41 41.793 25.04 20.0 $D_K \times 10^3$ 2.750 5 4.388 0 4.6018 5.73 $d_1 \times 10^9$ -142.3-20.90-7.08-19 $d_{2} \times 10^{9}$ -11.8-1.482-0.393577.925 8e 3609.482 48^g 3614.902 41ⁱ 3625.84^d ν_1 1353.404 66^t 1162.570 4ⁱ 1068^k 1238.624 60^h ν_2 575¹ ν_3 889.079 74^f 724.358 07^h 620.18^j H–OX Å 0.964^m 0.964 3^p 0.9643ⁿ 0.964 3° HO–X Å 1.442^{m} 1.6891ⁿ 1.827 9° 1.991 ∠H–O–X/° 97.2^m 102.96ⁿ 103.0° 105.4

TABLE IV. Comparison of ground state constants and vibrational frequencies (in cm⁻¹) and molecular structures for the hypohalous acids.

^aHOF rotational constants from Ref. 14. The values listed here have been converted to the symmetric top reduction (S) using the relations in Ref. 58.

^bHOCI rotational constants from Ref. 26.

^cHOBr rotational constants from Ref. 31.

^dFrom Table III.

^eReference 16.

^fReference 14. ^gReference 26.

^hReference 23.

ⁱReference 31.

^jReference 30. ^kReference 40.

¹Reference 39.

^mReference 11.

ⁿReference 24.

°Reference 31.

^pH-OI bond length constrained to value used for HOBr and HOCI.

the series from HOF to HOBr. Using this fact they predicted an OI bond length in HOI of 1.995 Å which is in reasonable agreement with our value of 1.991 Å.

It can be seen from Table IV that the quartic centrifugal distortion constants, D_J , D_{JK} , and D_K , show a monotonic variation with the changing mass of the halogen atom. If the HOX molecule is considered as a pseudodiatomic with the OH group treated as a single composite atom, then the D_J distortion constant for all of the hypohalous acids is well approximated by the relation linking the force constant and moment of inertia of a diatomic molecule to its centrifugal distortion constant,^{58,60}

$$D_e = \frac{4B_e^3}{\omega_e^2}.$$
(8)

The D_J distortion constants predicted by this simple relationship when ω_e is the HO–X vibrational frequency and B_e is taken as the mean of the measured ground state B and C rotational constants, $(B_0 + C_0)/2$, are in fair, quantitative agreement (~5%) with the measured values for all the hypohalous acids and also for HOD.^{61,62} The applicability of Eq. (8) to other polyatomic molecules which can be treated as pseudodiatomics was noted by Thomas *et al.* in their early study of the methyl halides.⁶³

Like the simple case for diatomic molecules, the distortion constants of asymmetric rotors can be derived from force constants and the derivatives of the inverse moment of inertia tensor with respect to internal coordinates;58,64 thus it is not surprising to find an empirical relationship between the distortion constants of a series of chemically similar molecules. Demaison et al.65 noted an empirical relationship between distortion and rotation constants which is broadly applicable to a large group of molecules and is helpful for obtaining initial estimates of at least the order of magnitude of the distortion constants. From Table IV, it is seen that the D_{JK} and D_K constants for the hypohalous acids also show a monotonic variation with the varying mass of the halogen atom. Using the functional form given in Eq. (7) as a guide, we have plotted in Fig. 7 log D_i (i=J,JK,K) vs log $4B_x^3/\omega_i^2$ where for $D_J, B_x = (B+C)/2$ and $\omega_i = \nu_3;$ for $D_{JK}, B_x = (B+C)/2$ and $\omega_i = \nu_2$; and for $D_K, B_x = A$ and $\omega_i = \nu_1$. These combinations of rotational constants and vibrational frequencies were chosen so that the plots all showed straight lines. Interestingly, the plots of the distortion constants done in this manner all have a common intersection. Also plotted in Fig. 7 are the points for HOD,^{61,62} which were calculated as for the hypohalous acids. The HOD centrifugal distortion terms are well predicted by the straight lines falling through the data for the hypohalous acids.



FIG. 7. Plot for all the hypohalous acids and also HOD of log D_i (i = J, JK, K) vs log $4B_x^3/\omega_i^2$, where for D_J , $B_x = (B+C)/2$ and $\omega_i = \nu_3$; for D_{JK} , $B_x = (B+C)/2$ and $\omega_i = \nu_2$; and for D_K , $B_x = A$ and $\omega_i = \nu_1$. HOD (\bullet); HOF (\bigcirc); HOCl (+); HOBr (\times); and HOI (*).

VII. CONCLUSIONS

The ν_1 fundamental, its overtones, and its hot bands for vibrationally hot HOI and DOI have been observed in emission. The anharmonicity of the OH(OD) stretch has been determined. Rotationally resolved spectra for the ν_1 fundamental and the $2\nu_1 - \nu_1$ hot band have been recorded at 0.031 cm⁻¹ resolution. These spectra have been analyzed and the derived rotational parameters are in good agreement with the other hypohalous acids. Finally we have commented on an empirical relationship linking the quartic centrifugal distortion constants for all the hypohalous acids and also those for HOD.

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