frequencies to those reported by Herzberg³⁴ (4139 and 4395 cm⁻¹, respectively).

Recent experimental findings³⁵ of the Neumark group raise the possibility that photodetachment may produce H_2F in more than one electronic state. At the equilibrium geometry of the $(H_2F)^$ complex we computed the vertical electron detachment energies to produce the ${}^{2}\Sigma$ and ${}^{2}\Pi$ states of H₂F neutral. At the CCSD(T) level of theory, we find that the vertical detachment energy to the ${}^{2}\Sigma$ neutral is 83.8 kcal/mol (3.63 eV). The ${}^{2}\Pi$ state of the neutral is 5.8 kcal/mol (0.25 eV) above the $^{2}\Sigma$ state.

These primary findings can be summarized as follows: (i) The H⁻HF complex does not exist. (ii) The H_2F^- complex is linear

and lies 31.3 kcal/mol below H⁻ + HF when zero-point corrections are considered. (Recall that basis set superposition errors amount to no more than 1 kcal/mol.) This complex has the vibrational frequencies and the geometry detailed in Table I. (iii) The $H_2F^$ complex is stable with respect to $H_2 + F^-$ by 4.7 kcal/mol when zero-point corrections are included. (iv) The reaction exothermicity for $H^- + HF \rightarrow H_2 + F^-$ is predicted to be -26.6 kcal/mol, including zero-point energies. The latter result is comparable to that computed by using tabulated energies of formation (-30 kcal/mol).

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Near-UV Absorption Cross Sections and Trans/Cis Equilibrium of Nitrous Acid

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The A ${}^{1}A'' \leftarrow X {}^{1}A'$ absorption spectrum of gaseous nitrous acid has been measured in the 300-400-nm range. Absolute cross sections were determined by a combination of gas-phase and wet chemical analysis. The cross sections of prominent bands are 25% larger than the recommended values of Stockwell and Calvert. The influence of spectral resolution on absolute and differential absorption cross sections was also investigated. The integrated band area of the $n\pi^*$ transition yields an oscillator strength $f = (8.90 \pm 0.36) \times 10^{-4}$, less than the reported liquid phase value of 2×10^{-3} . The equilibrium constant $K = p_{\text{trans}}/p_{\text{cis}}$, based on the assumption that the oscillator strength of the $n\pi^*$ transition is the same for both rotamers, was found to be 3.25 ± 0.30 at 277 K. This yields an energy difference ΔE between *trans*- and *cis*-HONO of -2700 J mol⁻¹ in the electronic ground state, and -6000 J mol^{-1} in the excited state.

1. Introduction

Although sources and typical ambient mixing ratios of gaseous nitrous acid in the atmosphere were unknown at the time, the photolysis of HONO¹

$$HONO + h\nu \to OH + NO$$
(1)

held a key position in early photochemical smog models,^{2,3} because it provided a rationale for the presence of OH radicals in polluted atmospheres. Later on, when the UV photolysis of ozone and the subsequent reaction $O(^{1}D) + H_{2}O \rightarrow 2OH$ was included in the kinetic schemes,^{4,5} the general importance of HONO as a source of OH radicals was called in question. Reaction 2,6 and other

$$NO + NO_2 + H_2O \leftrightarrow 2HONO$$
 (2, -2)

HONO-producing reactions of the NO_x-H₂O system,⁷ were found to be surface-catalyzed and too slow in the homogeneous gas phase to constitute significant sources of HONO under atmospheric conditions. Indirect evidence of unreasonably high HONO

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concentrations in polluted air was first obtained by a wet chemical technique.⁸ This method, as well as more recent denuder techniques,⁹ suffers severe interferences by other nitrogen compounds. Nighttime mixing ratios of up to 8 ppb HONO in very polluted air were unambiguously identified by long path differential optical absorption spectroscopy (DOAS) in the near-UV region,^{10,11} where HONO exhibits a characteristic banded absorption spectrum.¹² In cleaner air masses the mixing ratio always dropped below the detection limit of less than 100 ppt. As pointed out in a recent review article,¹³ the sensitivity of DOAS with respect to HONO is superior to most other analytical techniques.

Quantitative determination of HONO by DOAS requires absolute absorption cross sections and a well-resolved UV spectrum. However, such data are unavailable by standard laboratory techniques, because the gaseous compound can only be generated in the presence of other UV-absorbing species, 1,12 and the published absorption cross sections of HONO¹⁴⁻¹⁶ differ by as much as a factor of 4. The most recent absorption cross sections, which are recommended by the NASA Panel for Data Evaluation,¹⁷ were

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obtained by Stockwell and Calvert,¹⁶ who estimate their errors to be less than 10% at the band maxima. These authors reacted known amounts of NO and NO₂ with water vapor in the absorption cell of a commercial UV-vis spectrometer. Spectra were recorded when the thermodynamic equilibrium (2, -2) had established. The spectrum of HONO was deduced by subtracting the superimposed absorption spectra of NO₂, N₂O₄, and N₂O₃ from the composite spectrum. The equilibrium pressures of the interfering compounds were calculated from thermodynamic data.

The spectral measurements described in this paper pertain to highly diluted nonequilibrium mixtures of HONO, NO, and NO₂, in 1 atm of moist nitrogen. Under the experimental conditions, UV absorption by the dimers N_2O_4 and N_2O_3 were negligible, and only the superimposed NO₂ absorption spectrum had to be subtracted from the composite absorption spectrum. The spectral resolution and the signal-to-noise ratio were significantly better than in previous determinations, allowing a deconvolution of the spectrum to be made into separate contributions of the trans- and cis rotamers.

2. Experimental Section

2.1. The Reactor and Optical System. Absorption spectra of HONO in nitrogen were measured in an evacuable borosilicate glass reactor of 408-L volume. The entire setup was contained in a thermostated dark room which could be cooled to 0 °C. The optical system consisted of a deuterium lamp and quartz collimating optics, an optical path of 310 cm inside the reactor, folded once by means of a quartz corner cube prism reflector, a Jobin-Yvon HRS-2 monochromator with a 1800 lines/mm grating blazed for 250 nm, and an EMI 9635QB photomultiplier. The intensity of the deuterium lamp, determined before and after each set of measurements, exhibited a drift of less than 0.2%/h. The effective spectral resolution (=observed width (fwhm) of the 312.57-nm mercury line of a Pen-Ray calibration lamp) was 0.1 nm, and the wavelength reproducibility was better than 0.02 nm. Spectral scans, data acquisition, and data analysis were controlled by a microcomputer, using programs written with the ASYST software package. A scan speed of 25 nm min⁻¹ was used in all experiments. The photomultiplier output current was amplified, smoothed with a time constant of 0.1 s, and sampled at a rate of 1000 data min⁻¹ by the A/D converter of the computer.

2.2. Preparation of HONO. Before each experiment the dark room with the glass reactor was cooled overnight to 277 ± 2 K, because nonequilibrium concentrations of HONO were found to be more stable at reduced temperature. Nitrous acid vapor was prepared according to methods previously described in the literature:^{1,18,19} 25-50 mL of 0.5 M NaNO₂ solution was injected in portions of 2 mL into a Pyrex bulb which contained 50 mL of 5% H_2SO_4 . The gaseous products were allowed to expand directly, via a short Teflon tube, into the evacuated reactor, which was thereafter replenished to 1 atm with pure nitrogen. Starting concentrations were in the ranges of 65-175 ppm HONO, 125-240 ppm NO, and 60-150 ppm NO₂. The water vapor mixing ratio was approximately 5000 ppm, as deduced from the total pressure before addition of nitrogen to 1 atm. Interfering absorptions by N₂O₃ and N₂O₄, at equilibrium concentrations of <0.07 and <0.9 ppm, were negligible under these conditions. It could also be shown by exposing a microjet of distilled water to the gas mixture that no HNO_3 vapor was present in the reactor. The liquid jet, which selectively absorbs HNO₃ and other soluble trace gases,²⁰ was trapped after exposure, and analyzed by ion chromatography. Large amounts of NO₂⁻ from dissolved HONO were detected. NO_3^- was below the detection limit, which

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Figure 1. Absorption spectrum of HONO, spectral resolution 0.1 nm. Presented is a weighted average of 24 individual spectra covering concentrations from 1.3×10^{14} to 44.8×10^{14} cm⁻³.

amounted to less than 1% of the nitrite concentration.

2.3. Analytical Techniques. The concentrations of HONO in the reactor could be obtained by difference from measurements of NO, NO₂, and total NO_x (=NO + NO₂ + HONO):

$$[HONO] = [NO_x] - [NO] - [NO_2]$$
 (3)

NO was measured with a dedicated NO/O₃ chemiluminescence detector designed for very low sampling rates (8 mL min⁻¹). NO₂ was determined in situ by laser-induced fluorescence.²¹ The beam of a HeNe laser, $\lambda_{exc} = 442$ nm, was directed through a Brewster window along the axis of the reactor and dumped into a light trap at the other end. A portion of the fluorescent beam was focused on the photocathode of a cooled RCA 31034 photomultiplier used in the photon-counting mode. Scattered light was blocked with a suitable liquid solution filter. Both detectors were routinely calibrated by injecting known concentrations of the pure gases in nitrogen into the reactor. For the determination of total NO_x , the trace gases were converted to nitrate in aqueous solution, which was measured by ion chromatography. Gas samples for analysis were drawn from the reactor into evacuated glass bulbs of 125-mL volume. The bulbs were treated with 10 mL of distilled water and enough ozonized oxygen to ensure complete oxidation and hydrolysis of the nitrogen oxides. Systematic analytical errors were minimized by cross-calibrating the NO and NO₂ detectors with the wet chemical method, following exactly the same sampling/hydrolysis procedure as for total NO_x.

3. Results

3.1. Absorption Spectra. Each experimental run was carried out at 277 ± 2 K in the following order:

(a) filling of the reactor with pure nitrogen; acquisition of the deuterium lamp spectrum;

(b) calibration of the NO detector, calibration of the NO_2 detector, and acquisition of an NO_2 absorption spectrum;

(c) evacuation of the reactor and acquisition of the deuterium lamp spectrum;

(d) preparation of HONO as described in section 2.2; addition of nitrogen to 1 atm;

(e) repetitive scanning of spectra; between scans NO and NO_2 measurements; gas sampling into five bulbs for total NO_x determinations by ion chromatography, as described in section 2.3; (f) repetition of steps a and b.

By dividing the lamp spectrum $I_0(\lambda)$ through the spectra $I(\lambda)$ recorded in stage e and calculating ln $[I_0(\lambda)/I(\lambda)]$, we obtained the composite absorption spectra of HONO and NO₂. These were converted into absorption spectra of pure HONO by subtracting NO₂ from each composite spectrum. Because HONO decayed slowly during the measurements (see below), NO₂ absorbances were scaled with the interpolated real time NO₂ concentrations. The procedure worked extremely well, because all spectra, in-

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TABLE I: HONO Absorption Cross Sections $\sigma [10^{-19} \text{ cm}^2]^{a}$

λ, nm	σ	λ, nm	σ	λ, nm	σ
300.0	0.00	333.5	0.83	366.5	2.20
300.5	0.02	334.0	0.96	367.0	3.02
301.0	0.00	334.5	0.99	367.5	4.23
301.5	0.00	335.0	0.96	368.0	5.20
302.0	0.00	335.5	0.83	368.5	5.11
302.5	0.02	336.0	0.72	369.0	3.88
303.0	0.05	336.5	0.57	369.5	2.63
303.5	0.06	337.0	0.53	370.0	1.78
304.0	0.08	337.5	0.59	370.5	1.32
304.5	0.11	338.0	1.00	371.0	1.13
305.0	0.13	338.5	1.90	371.5	1.04
305.5	0.14	339.0	1.88	372.0	1.00
306.0	0.09	339.5	1.32	372.5	0.90
306.5	0.06	340.0	1.00	373.0	0.77
307.0	0.04	340.5	1.01	373.5	0.68
307.5	0.06	341.0	1.70	374.0	0.62
308.0	0.11	341.5	3.58	374.5	0.51
308.5	0.14	342.0	3.86	375.0	0.53
309.0	0.20	342.5	2.47	375.5	0.52
309.5	0.19	343.0	1.49	376.0	0.53
310.0	0.13	343.5	1.08	376.5	0.52
310.5	0.13	344.0	0.97	377.0	0.50
311.0	0.19	344.5	1.02	377.5	0.53
311.5	0.29	345.0	1.09	378.0	0.58
312.0	0.28	345.5	1.14	3/8.3	0.00
312.5	0.22	340.0	1.23	379.0	0.80
313.0	0.22	340.3	1.17	3/9.3	0.09
313.3	0.28	347.0	1.04	380.0	1.02
214.0	0.30	347.3	0.74	380.5	1.05
215.0	0.39	346.0	0.91	381.5	1.15
315.5	0.30	340.0	0.88	382.0	1.55
316.0	0.22	349.5	0.73	382.0	1.35
316.5	0.14	350.0	1 1 2	383.0	2 10
317.0	0.20	350.5	1.82	383.5	2 33
317.5	0.48	351.0	2 12	384.0	2.41
318.0	0.56	351.5	1.78	384.5	2.30
318.5	0.45	352.0	1.55	385.0	2.03
319.0	0.36	352.5	1.57	385.5	1.68
319.5	0.34	353.0	1.91	386.0	1.34
320.0	0.49	353.5	3.23	386.5	1.07
320.5	0.72	354.0	5.81	387.0	0.90
321.0	0.78	354.5	5.80	387.5	0.74
321.5	0.60	355.0	3.64	388.0	0.56
322.0	0.49	355.5	2.11	388.5	0.44
322.5	0.46	356.0	1.41	389.0	0.34
323.0	0.51	356.5	1.19	389.5	0.29
323.5	0.64	357.0	1.17	390.0	0.27
324.0	0.71	357.5	1.23	390.5	0.24
324.5	0.62	358.0	1.20	391.0	0.20
325.0	0.50	358.5	1.10	391.5	0.18
325.5	0.36	359.0	1.04	392.0	0.15
326.0	0.29	359.5	1.01	392.5	0.14
326.5	0.38	360.0	0.90	393.0	0.11
327.0	0.66	360.5	0.86	393.5	0.03
327.5	1.13	361.0	0.83	394.0	0.06
328.0	1.1/	301.3	0.01	374.3	0.10
328.3	0.83	302.0	0.80	393.0	0.10
229.0	0.01	302.3	0.07	373.3 206 0	0.09
329.3	1 1 1	363.0	1 20	206 5	0.04
320.0	1.11	364 0	1.20	307 0	0.02
330.5	1 79	364.5	1.40	397.5	0.09
331.5	1.28	365.0	1.68	398.0	0.13
332.0	0.87	365.5	1,69	398.5	0.11
332.5	0.74	366.0	1.83	399.0	0.02
333.0	0.76				-

 a The cross sections are averaged over 0.5 nm intervals. λ [nm] are the center wavelengths.

cluding the NO_2 reference spectrum, were recorded at the same temperature, spectral resolution, and scan speed. The absorption spectrum of HONO in terms of cross sections was derived from the residual absorbance by dividing by the optical path length and the HONO concentration. Again, interpolated real time HONO concentrations were utilized.



Figure 2. Beer plot for five prominent band maxima of HONO: (+) $368.2 \text{ nm} (\times 2)$; (#) 354.2 nm; (O) 341.7 nm; (*) 384.0 nm; (×) $330.7 \text{ nm} (\times 0.5)$.

TABLE II: Absorption Cross Sections of HONO from the Slopes of Beer Plots of Prominent Band Maxima^a

20 ^{v'} band	position, cm ⁻¹	σ (this work), 10^{-20} cm^2	$\sigma(ref), 10^{-20} cm^2$	diff, %
$v_{2}' = 0$	26 03 5	24.2 ± 1.3^{b}	19.9	-18
$v_{2}' = 1$	27135	55.1 ± 1.5	45.0	-18
$v_{2}' = 2$	28 220	64.2 ± 2.4	49.6	-23
$v_{2}' = 3$	29 249	42.1 ± 1.5	33.5	-21
$v_{2}' = 4$	30 227	19.8 ± 1.1	(13.8)	(-30)

^a Data from this work pertain to 0.1-nm spectral resolution, unless otherwise noted. The uncertainties are 3σ standard deviations of the slopes, Figure 2. σ (ref) are from Table 2 and Figure 3 of Stockwell and Calvert.¹⁶ The last column lists the difference (in %; our data = 100%) between the cross sections in columns 3 and 4. ^b Resolution 0.8 nm.

TABLE III: Differential Absorption Cross Sections $\Delta \sigma$, Referring to Adjacent Maxima and Minima^a

λ _{min} , nm	λ _{max} , nm	$\Delta\sigma$, 10 ⁻²⁰ cm ²	lit. data	
352.2	354.2	49.4 ± 1.7	120	
356.9	354.2	52.8 ± 1.7	42	
361.8	354.2	56.8 ± 2.1		
361.8	368.2	47.5 ± 1.0	33.70	

^aSpectral resolution 0.1 nm. ^bPerner and Platt.¹⁰

A total of 24 HONO spectra from four experimental runs, covering the concentration range of $(1.35-4.55) \times 10^{15}$ cm⁻³ HONO, were stored in the computer memory. Figure 1 shows a weighted average of all 24 absorption spectra. The spectral resolution below 375 nm is 0.1 nm. Above this wavelength the resolution had to be reduced to 0.8 nm to yield a smooth spectrum, because the multiline structure of the deuterium lamp gave rise to oscillations in the ratioed high-resolution spectra. The change from 0.1 to 0.8 nm spectral resolution had little effect on the cross sections in this part of the spectrum.

The absorption cross sections of HONO obtained in this work are listed in Table I. Averages over 0.5-nm intervals are presented for each center wavelength.

3.2. Effects of Spectral Resolution. The spectrum of HONO is truly continuous in the investigated spectral range, and its structure has been fully resolved at our spectral resolution of 0.1 nm.¹² Beer plots of absorbance versus HONO concentration should therefore be linear. This is confirmed by the plots shown in Figure 2, which pertain to the maxima of five prominent bands. Note that the data from all 24 spectra are included.

The slopes of the least-squares-fitted straight lines through the data in Figure 2 yield absorption cross sections for the band maxima, which are in good agreement with the spectrum shown in Figure 1. Results are listed in Table II. The uncertainty ranges $(3\sigma \text{ standard deviations})$ convey an impression of the overall precision of our measurements. Additional systematic errors, which would affect the accuracy of our absorption cross sections,



Figure 3. Beer plot for differential absorption cross sections $\Delta \sigma$ of HONO: (×) (×2), $\lambda_{max} = 368.2 \text{ nm}$, $\lambda_{min} = 361.9 \text{ nm}$; (O) $\lambda_{max} = 354.2 \text{ nm}$, $\lambda_{min} = 356.9 \text{ nm}$.



Figure 4. Influence of spectral resolution on effective absorption cross sections of HONO: (#) σ (λ = 354.2 nm); (+) σ (λ = 368.2 nm); (O) (λ_{max} = 354.2 nm, λ_{min} = 356.9 nm); (×) $\Delta\sigma$ (λ_{max} = 368.2 nm, λ_{min} = 361.8 nm).

are estimated to be comparable to the statistical 3σ errors.

Differential absorption cross sections $\Delta\sigma$ (defined here as the differences between absorption cross sections of well-resolved spectral maxima and adjacent minima) are needed for HONO determinations by the DOAS technique. Values of $\Delta\sigma$ can likewise be obtained from the slopes of Lambert-Beer plots, as depicted in Figure 3. We have listed suitable differential cross sections for the DOAS technique in Table III. Note that the Beer plots of the band maxima, Figure 2, and of the differential absorptions, Figure 3, are scattered statistically around straight lines through the origin, indicating negligible interference of unknown absorbing impurities.

When published absorption cross sections are utilized to measure low HONO concentrations by DOAS, the effect of reduced spectral resolution must be considered. For very small absorbances Beer's law may be linearized (N = number density of the absorbing molecule; x = absorbing path):

$$I/I_0 = \exp(-\sigma Nx) \approx 1 - \sigma Nx$$
 (4)

When the optical resolution is insufficient to resolve narrow features in the absorption spectrum, σ in eq 4 must be replaced by an average σ , weighted with the instrumental slit function. We have simulated this effect by smoothing the original high-resolution spectrum, Figure 1, with a Gaussian filter function. The result is shown in Figure 4. Note that the effect of optical bandwidth $\Delta\lambda$ on σ and $\Delta\sigma$ is not negligible for instrumental bandwidths $\Delta\lambda \ge 0.5$ nm when narrow spectral features are observed, as is the case in DOAS.

3.3. Reaction Rates. Figure 5 shows that HONO decayed slowly in our glass reactor. Chan et al.^{18,19} assumed that the decay of HONO in their system was governed by the homogeneous reactions 2 and -2. The solid lines in Figure 5 are computer fits through our data using the same mechanism and the reported



Figure 5. Decay of HONO, four experiments in the borosilicate glass reactor at 277 K. The solid lines are computer fits, assuming the simple mechanism (2,-2) and an equilibrium constant $K_2 = 4.55$.¹⁶ The fits yielded the following effective rate constants k_{-2} (10⁻⁵ ppm⁻¹ min⁻¹): (*) 3.4; (O) 1.9; (+) 1.7; (#) 3.0.



Figure 6. Absorption spectrum of HONO on a wavenumber scale, showing $2_0^{b'}$ progressions of *trans*- and *cis*-HONO. The assignment of the weaker $4_0^{1}2_0^{b'}$ progression is based on ref 12 and recent theoretical work.²²

equilibrium constant $K_2 = k_2/k_{-2}$,¹⁶ while treating k_{-2} as a free parameter in the closed-form solution. The least-squares fitting routine yielded formal rate constants k_{-2} ranging from 1.7×10^{-5} to 3.4×10^{-5} ppm⁻¹ min⁻¹, nearly 2 orders of magnitude lower than the room temperature value of $(1.4 \pm 0.4) \times 10^{-3}$ ppm⁻¹ min⁻¹ reported by Chan et al.^{18,19} Some of the scatter in our k_{-2} may be due to poor estimates of the water vapor concentration. Our lowest value, $k_{-2} = 1.1 \times 10^{-20}$ cm³ s⁻¹ in molecular units, is close to the upper bound of 1×10^{-20} cm³ s⁻¹ reported by Kaiser and Wu⁶ for much smaller Pyrex vessels. These authors concluded that the reaction is essentially heterogeneous.

4. Data Analysis and Discussion

4.1. Band Assignment and Oscillator Strength. The A ${}^{1}A'' \leftarrow X {}^{1}A'$ spectrum of HONO in the 300-400-nm range has been assigned to an $(n_0\pi^*)$ absorption localized on the N=O chromophore. The weakening of this bond in the excited state gives rise to a long progression in the N=O stretching vibration v_2' .¹² Portions of the excited-state potential hypersurface have been calculated by Suter and Huber²² and by Henning et al.,²³ who have been able to simulate salient features on the absorption

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TABLE IV: Parameters for Fitting the $2_0^{v'}$ Progressions of the Composite *cis*- and *trans*-HONO Spectrum, Figure 8^a

quantum no. v2'	band	position, ^{b} cm ⁻¹	$h_{\rm max}, 10^{-20} {\rm cm}^2$	bandwidth, fwhm, cm ⁻¹	
		trans-Nitrous	Acid		
0	26 0 3 5	(26034)	22.9	293	
1	27153	(27 1 50)	53.25	177	
2	28 2 20	(28 225)	63.0	124	
3	29 249	(29 231)	40.7	116	
4	30 2 2 7	(30 231)	18.5	138	
5	31158	(31 175)	7.5	167	
6	32 076	(32075)	2.75	167	
		cis-Nitrous A	cid		
0	26312	(not resolved)	3.95	293	
1	27 430	(27 420)	10.6	177	
2	28 496	(28 495)	18.0	124	
3	29 51 3	(29 518)	18.7	116	
4	30 502	(30 505)	11.1	138	
5	31 4 5 6	(31 461)	5.0	167	
6	32 344	(32 350)	1.75	167	

^a The band positions used for the fit, column 2, differ slightly from the band maxima, which agree better with the band maxima of King and Moule.¹⁶ ^b Numbers in parentheses: data of King and Moule.¹²

spectrum. They conclude that the shoulders on the low-energy side of the main $2_0^{t'}$ progression, previously interpreted as hot bands involving a lower state frequency of 620 cm⁻¹,¹² should rather be assigned to combination bands in which one quantum of the upper state N-O stretching vibration v_4' is simultaneously excited. We have adopted this assignment in Figure 6, which shows our absorption spectrum on a wavenumber scale. The other progression, which is shifted 280 cm⁻¹ to higher energies and does not appear in the theoretical spectrum of Suter and Huber,²² has been assigned to *cis*-HONO by King and Moule.¹²

The absence of rotational structure in the vibronic bands¹² is due to extremely rapid vibrational predissociation of the N–O bond in the excited state, yielding OH + NO.²² The band structure has been interpreted in terms of scattering resonances, resulting from a shallow well in the excited-state potential energy surface, which was calculated as function of $R_{N=O}$ and R_{N-O} .²² Calculated contour plots of the potential surface versus other bond length combinations²² show that the O–H bond is stable in the excited state, explaining why photodissociation into H + NO₂ does not occur in this spectral range.¹ The $n_0\pi^*$ absorption of HONO is well separated from other electronic transitions of the same molecule, which start to absorb strongly below 270 nm.¹⁵ The oscillator strength f of the entire band system may thus be determined as a measure of the optical absorption strength which is independent of the spectral resolution employed^{24,25}

$$f = \frac{4\epsilon_0 mc^2}{e^2} \int \frac{\sigma}{\lambda^2} d\lambda \quad \text{(in SI units)} \quad (5)$$

 ϵ_0 is the permittivity of vacuum; *m* and *e* are the mass and charge of an electron; and *c* is the speed of light.

Integration of our spectrum over the wavelength range 300-400 nm yielded $f = (8.90 \pm 0.36) \times 10^{-4}$. A somewhat larger oscillator strength, f = 0.002, has been reported for HONO in the aqueous phase.¹²

4.2. Comparison with Previous Absorption Spectra. The good agreement of our band positions, Table IV, with the wavenumbers reported by King and Moule¹² is gratifying, confirming the excellent reproducibility of our monochromator. It also indicates that the quantitative subtraction of the complex NO₂ spectrum from our composite absorption spectrum has been successful.

A superposition of our absorption spectrum with the spectrum of Stockwell and Calvert is shown in Figure 7. A weak progression of bands in the valleys between the $4_0^{\nu'}$ progressions of



Figure 7. Comparison of HONO absorption spectra: (+) absorption cross sections tabulated in 1-nm intervals;¹⁶ neat solid line: this work, 0.1 nm resolution.



Figure 8. (a) Experimental (solid line) and synthetic absorption spectrum of HONO (dashed line), composed of Lorentz-shaped $2_0^{o'}$ bands of both rotamers; fitting parameters listed in *Table* 11. (b) Residual spectrum obtained by subtracting the synthetic spectrum from the experimental one.

trans- and cis-HONO, which has been resolved in this and other more recent work,²² is wiped out in the spectrum of Stockwell and Calvert. Our absolute absorption cross sections of prominent band maxima are compared with the results of these authors in Table III (cf. section 3.2). Their cross sections are approximately 20% lower than our data, suggesting that a systematic error was involved. [This average relative reduction does not include cross sections below 331 nm where the spectral features are inconsistent with our spectrum, Figure 1, and with other work.^{12,22}] We speculate that Stockwell and Calvert have subtracted too much NO₂ absorption from their composite spectrum. This would also explain the 18% lower oscillator strength, $f = 7.3 \times 10^{-4}$, based on the absorption cross sections in Table 2 of ref 16, which should be independent of the spectral resolution employed.

4.3. The trans-HONO-cis-HONO Equilibrium. It is now well established that the trans rotamer of HONO is energetically favored, and thus more abundant than the cis rotamer. Experimental estimates of the energy difference ΔE between the rotamers, mainly from temperature dependence measurements of infrared band intensities over a very limited temperature range, are $\Delta E \equiv E_{\text{trans}} - E_{\text{cis}} = -506 \pm 250 \text{ cal/mol},^{26} \Delta E = -531 \pm 1000 \text{ cal/mol},^{27} \text{ and } \Delta E = -404 \pm 100 \text{ cal/mol}$ (from microwave line

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intensities²⁸), with a barrier to rotation from trans to cis in the order of 9.7 kcal/mol.^{29,30} Calculations of ΔE by ab initio methods have also been reported.^{30,31} The most recent theoretical estimate is $\Delta E = -642$ cal/mol.

Most of the cis and trans $2_0^{v'}$ bands in *Figure* 6 are sufficiently well separated to deconvolute the spectrum into a superposition of Lorentz-shaped bands, Figure 8, which is the predicted line shape of scattering resonances.²³ All bands were fitted simultaneously, disregarding the contributions of $20^{0'}$ bands of both rotamers. The heights and widths of the bands and the band positions were varied until a satisfactory fit was obtained. The unknown half-widths of the congested cis bands at 26312 and 27 430 cm⁻¹, which could not be determined from the spectrum, were assumed to equal those of the corresponding trans bands. The parameters which yield the best fit, dashed contour in Figure 8a, are listed in Table IV. Attempts to fit the spectrum assuming Gaussian-shaped band contours were unsuccessful. The synthetic spectrum accounts for 84% of the oscillator strength. The residual spectrum, Figure 8b, consists of $2_0^{\nu'}4_0^{-1}$ combination bands²² and other unassigned bands.

An interesting feature of the synthetic spectrum is the smooth variation of the bandwidth (fwhm), from a maximum of 293 cm⁻¹ at $v_{2}' = 0$ to a shallow minimum of 116 cm⁻¹ at $v_{2}' = 3$. This opposes the theoretically predicted trend from a very narrow (0,0)band to larger than the observed widths at $v_{2}' \ge 2.2^{3}$ We also note that the relative Franck-Condon distributions of the trans and cis rotamers are different. Such differences cannot be explained by the published potential energy surfaces^{22,23} which do not differentiate between the rotamers.

The parameters listed in Table IV can be utilized to apportion fractional oscillator strengths f^* to the $2_0^{o'}$ progressions of the cis and trans rotamers separately, by integrating over the band areas:

$$f^* N_{\text{trans}} = \frac{4\epsilon_0 mc^2}{e^2} N_{\text{trans}} \int \sigma_{\text{trans}} d(1/\lambda)$$
(all $2_0^{e'}$ bands of *trans*-HONO) (6a)

= const ×
$$\sum_{i=0}^{6} h_{\max,i}$$
 fwhm_i
(summation over all trans bands) (6b)

Summing over the $2_0^{\nu'}$ progressions of the trans and cis rotamers yielded the following ratio of band areas:

$$\frac{f^* N_{\rm trans}}{f^* N_{\rm cis}} = 3.25 \pm 0.30 \tag{7}$$

The error limits are estimates based on acceptable variations of the fitting parameters in Table IV. If one makes the reasonable assumption that the A ${}^{1}A'' \leftarrow X {}^{1}A'$ transitions of both rotamers have identical oscillator strengths, and that the partitioning of oscillator strength between the $2_0^{o'}$ progression and the residual spectrum, Figure 8b, is the same for both isomers, this ratio is equal to the equilibrium constant $K = N_{\text{trans}} \cdot N_{\text{cis}}$ at the temperature of our measurements, $T = 277 \pm 2$ K:

$$K = N_{\rm trans} / N_{\rm cis} \approx 3.25 \pm 0.30 \tag{8}$$

The Gibbs free energy difference between the rotamers, $\Delta G_{\text{trans-cisy}}$ is obtained from the equilibrium constant K as follows:

$$\Delta G = -RT \ln \frac{N_{\text{trans}}}{N_{\text{cis}}}$$
$$= -649^{+55}_{-50} \text{ cal mol}^{-1} \qquad (9)$$

A room temperature entropy difference of $\Delta S = S_{\text{trans}} - S_{\text{cis}} =$ +0.01 eu between the rotamers has been calculated by McGraw



Figure 9. Photoaction spectrum of HONO, eq 11, using absorption cross sections from Table I and a field-measured irradiance spectrum,35 resolution 1.6 nm, solar zenith angle 40.8°, ozone column 324 Dobson units.

et al.²⁷ It leads to a marginally smaller energy difference ΔE between the rotamers:

1

$$\Delta E = \Delta G + T \Delta S = -646^{+55}_{-50} \text{ cal mol}^{-1}$$
(10)

The coincidence of our ΔE with the most recent theoretical result,³⁰ which does not, however, include a difference of about 75 cal mol⁻¹ between the zero-point energies of the rotamers (vibrational frequencies from Deeley and Mills³²) is considered to be accidental. Our ΔE is larger than, but still within the error limits of, most previous experimental values.

From the obtained Gibbs free energy difference, $\Delta G_{\text{trans-cis}}$, the effect of temperature on the absorption spectrum can be studied by calculating synthetic spectra for different values of the equilibrium constant K_{T} . We conclude that the cross sections of prominent trans-HONO bands decrease by less than 2% when the temperature is raised from 277 to 298 K.

The energy separation ΔE^* between the excited-state hypersurfaces of the trans and cis isomers is obtained, relative to ΔE in the ground state, from the shift of 276 \pm 11 cm⁻¹ between corresponding cis and trans bands of the 2_0^{ν} progressions, Figure 6, which yields $\Delta E^* = 1435 \pm 90$ cal mol⁻¹. Possible reasons for the reduced stability of the cis isomer in the excited state have been discussed by King and Moule.¹²

4.4. The Photolysis Rate of HONO. Previous authors have utilized their absorption spectra to estimate photolysis rate coefficients j [s⁻¹] of HONO in the atmosphere:

$$j = \sum_{300-400 \text{ nm}} \sigma_i I_i \Phi_i \Delta \lambda_i \tag{11}$$

 I_i is the actinic flux (photons cm⁻² s⁻¹ nm⁻¹); Φ_i is the quantum yield, = 1.00 for HONO; $\Delta \lambda_i$ is the wavelength interval (nm).

The function $\sigma_i I_i \Phi_i \Delta \lambda_i$ is called the photoaction spectrum. The actinic fluxes I_i , which have been published by Peterson³³ for $\Delta\lambda$ = 5 nm intervals, do not resolve the pronounced Fraunhofer structure in this region of the solar spectrum.³⁴ We have therefore utilized UV irradiances³⁵ which were measured with 1.6-nm spectral resolution under clear-sky conditions at a solar zenith angle of $z = 40.8^{\circ}$, ozone column 324 Dobson units, to calculate the photoaction spectrum of HONO, Figure 9. The band structure of the spectrum is not seriously affected by the superimposed Fraunhofer structure, but the "center of gravity" is shifted to longer wavelengths. The summation¹¹ yields a photolysis rate coefficient $j = 8.0 \times 10^{-4} \text{ s}^{-1}$. Note that this value is based on *irradiances* rather than on actinic fluxes, which underrate the contribution of nonperpendicular radiation by the $\cos z$ factor. Combining our absorption spectrum with Peterson's tabulated actinic fluxes yields $j = 15.2 \times 10^{-4} \text{ s}^{-1}$ for zero albedo and $z = 40^{\circ}$ ($j = 16.5 \times 10^{-4}$ s^{-1} "for best estimate surface albedo"). The corresponding photolysis rate coefficient shown in Figure 4 of ref 16 for unspecified

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albedo is $i = 12.6 \times 10^{-4} \text{ s}^{-1}$, 17% (24%) lower than our value.

5. Summary and Conclusions

A UV absorption spectrum of pure gaseous HONO has been obtained at a spectral resolution of 0.1 nm, by careful subtraction of NO₂ from composite spectra of highly diluted HONO/NO/ NO_2/H_2O mixtures in nitrogen. Existing uncertainties in absolute absorption cross sections could be reduced to approximately $\pm 5\%$ or $\pm 5 \times 10^{-21}$ cm², whichever is greater, in the investigated spectral range. Owing to recent theoretical work, the photochemistry of HONO, particularly the continuous nature of the spectrum and the line shapes of bands, are now well established. Salient features of the spectrum have been reproduced by a synthetic spectrum composed of Lorentzian bands of the trans and cis rotamers, which

form progressions of the upper state N=O stretching vibration, v_2' . Deconvolution of the spectrum into progressions of the trans and cis rotamers yields an estimate of the equilibrium constant $N_{\rm trans}/N_{\rm cis} = K$, corresponding to an energy difference $\Delta E = -646$ cal mol⁻¹ (2700 J mol⁻¹) between the rotamers, in good agreement with a recent theoretical estimate.

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A Molecular Dynamics Study of Pressure Effects on Solvation and Optical Spectra: The Ground and Excited States of Formaldehyde in Water

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Molecular dynamics simulations of formaldehyde in liquid water have been carried out at high pressures (1 and 10 kbar). The results of three sets of simulations are reported corresponding to the equilibrium solvation of this model dipolar solute in the ground state $(^{1}A_{1})$, the first excited singlet state $(^{1}A'')$, and the nonequilibrium solvation following a simulated electronic excitation. The high-pressure simulations are compared with the results at low pressure (1 bar) reported previously. The changes in the structure of the solvation shell of the ground-state species as the pressure is increased to 10 kbar are relatively small. In contrast, there are more substantial changes in the solvation structure of the excited-state species with increasing pressure. At low pressure, the solvation shell surrounding the ${}^{1}A''$ state is disordered relative to that of the ground state. High pressure induces the formation of a distinct solvation shell around the formyl oxygen in the excited state. The waters in the first solvation shell have rotated by 180°, however, with respect to their preferred orientation in the ground state. Because of compensating effects involving different atoms of the solute, the changes in the total solvation energies of the ground and excited states with pressure are small, leading to a small pressure-induced blue shift in the optical absorption. These results indicate that it is important to account for the extended shape and charge distribution of the solute and the molecular nature of the solvation shell when considering pressure-induced effects on optical spectra. The nonequilibrium solvation dynamics corresponding to a laser-induced excitation is simulated by following 80 trajectories which start from different configurations on the ground-state surface. At high pressure, the rotational relaxation of waters in the first solvation shell is an order of magnitude slower than the solvent response at low pressure. The use of simulations to aid in developing molecular models for "pressure tuning spectroscopy" experiments is discussed.

Introduction

The analysis of solvent effects on optical absorption bands is a classical method that has long been used to study the energetics and dynamics of solvation.¹⁻⁵ In the simplest description of the process, an optical excitation leads to a sudden charge redistribution within the solute; the differential solvation between the two electronic states results in an absorption line shift. After excitation, the solute and solvent begin to relax and this leads to a time-dependent fluorescence shift. The intimate relationship that exists between effects observed in time-resolved fluorescence experiments and electron transfer has been discussed by several authors.^{2,5-9} Several lines of theoretical analysis point to the important role played by the first solvation shell in the solvent

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response following an optical excitation.⁷⁻¹⁵ We have been engaged in a series of calculations on the effects of solvation on the electronic and spectral properties of model solute-solvent systems.^{14a-d} In a recent communication, we reported the results of molecular dynamics simulations of the time-resolved fluorescence from the first excited singlet state $({}^{1}A'')$ of a model dipolar solute, formaldehyde, in water.^{14d} In this paper we extend this work to simulations of high-pressure effects on the solvation of the ground

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