# S<sub>1</sub> POTENTIAL ENERGY SURFACE OF HONO: ABSORPTION SPECTRUM AND PHOTODISSOCIATION

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Received 17 November 1988

The molecular geometry of cis- and trans-HONO in the S<sub>0</sub> and S<sub>1</sub> states as well as the S<sub>1</sub>( $n\pi^*$ )  $\leftarrow$  S<sub>0</sub> transition energy were calculated by ab initio methods (CI, MCSCF). Together with S<sub>1</sub>-potential energy surface calculations in three dimensions ( $R_{O-N}$ ,  $R_{N-O}$ ,  $R_{O-H}$ ) the absorption spectrum and the photodissociation of trans-HONO into OH and NO are discussed.

# 1. Introduction

If excited to the first electronically excited  $(A^{\dagger}A'')$  state, nitrous acid (HONO) dissociates producing ground state OH and NO radicals according to the scheme

$$HONO(\tilde{X}^{I}A') \xrightarrow{h\nu} HONO(\tilde{A}^{I}A'')$$
$$\rightarrow OH(X^{2}\Pi) + NO(X^{2}\Pi).$$
(1)

This prompt dissociation process ( $\approx 100$  fs) has been investigated for trans-HONO in considerable detail using the LIF technique to probe the OH as well as the NO fragment [1,2]. While OH is created translationally hot but vibrationally and rotationally cold, NO exhibits a high degree of excitation in the vibrational and rotational motions. Moreover, electronic ( $\Lambda$ -doubling) and rotational alignment measurements carried out on both fragments show the dissociation process to proceed in the plane of the parent molecule [1,2].

Based on a two-dimensional S<sub>1</sub>-potential energy surface, calculated by an MCSCF ab initio method with variation of the coordinates  $R_{\text{O-N}}$  and  $R_{\text{N-O}}$ , a quantum mechanical study of the photodissociation of trans-HONO was performed [3]. The dominant bands of diffuse structure in the S<sub>1</sub>( $n\pi^*$ )  $\leftarrow$  S<sub>0</sub> absorption spectrum could be attributed to scattering resonances resulting from the shallow potential well in the S<sub>1</sub> surface close to the Franck-Condon region. The fragmentation occurs predominantly via vibrational predissociation on the S<sub>1</sub> surface by transferring one quantum of the N=O stretching vibration into the dissociation mode. Furthermore, classical and quantum mechanical calculations predict a relatively high vibrational excitation of the NO fragment which is strongly dependent on the initial vibronic state. The results are very similar to those found for the photodissociation of methyl nitrite,  $CH_3ONO \rightarrow CH_3O + NO$  [4-6].

The present communication is concerned with the OH fragment and its almost unexcited internal degrees of freedom. Using the same MCSCF method as before, we carried out ab initio calculations of the S<sub>1</sub> potential energy surface (PES) of trans-HONO by changing the coordinates  $R_{O-N}$  and  $R_{O-H}$  for two fixed N=O bond lengths. The distinct difference between the PES  $(R_{O-N}, R_{N=O})$  and PES  $(R_{O-N}, R_{O-H})$  in the Franck-Condon region and along the exit channel make the contrasting behavior of the OH and the NO fragment with respect to vibrational (and rotational) excitation clearly evident. The vibrational predissociation process of HONO in the  $S_1$  state is thus characterized by a strong vibrational-translational interaction along the exit channel of NO in contrast to a very weak one along the OH channel.

#### 2. Method of calculation

HONO is a planar molecule in the  $S_0$  and  $S_1$  state and belongs to the C<sub>s</sub> symmetry group. The ground

0 009-2614/89/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) state equilibrium geometries of its trans and cis conformers were optimized using the single-reference CISD (CI with single and double excitation) method [7] including the Davidson correction [8] as well as the CEPA-1 [9] methods (cf. table 1). The results of a GAUSSIAN 82 calculation (MP4/6-311G\*\*) [10], although in good agreement with the experimental geometry, were not considered further since the relative energies of the cis and trans forms were inferior to those of the CI and CEPA-1 calculations. Furthermore, an optimization of the S<sub>1</sub> equilibrium geometry of the trans rotamer was also performed using the MCSCF method described below.

The potential energy surface of the S<sub>1</sub> state was calculated as a function of the O-N and O-H bond lengths, keeping the rest of the geometry fixed at the experimentally determined parameters for the electronic ground state. As previously, we employed the MCSCF program developed by Shepard et al. [11]. The DZ+P standard Huzinaga basis set [12] consisted of a set (10s, 6p, 1d) for the N and O atoms contracted to [4s, 2p, 1d] and a set (4s, 1p) for the H atom contracted to [2s, 1p]. The orbital exponents were taken as  $\alpha_0 = 1.25$ ,  $\alpha_N = 0.8$  and  $\alpha_H = 0.7$ .

This basis set gives rise to 37 orbitals of a' symmetry and 13 ones of a" symmetry. In the electronic ground state 10 orbitals of a' and 2 of a" symmetry are occupied. Hence, we used the same basis set as in our previous calculations [3] and also made the same choice for the active space.

In addition, the excitation energy for the  $S_1 \leftarrow S_0$  transition at fixed ground state equilibrium geometry (Franck-Condon transition) was calculated by applying the CI optimized geometry (cf. table 1).

# 3. Result and discussion

#### 3.1. Absorption spectrum

The spectrum of HONO in the near-ultraviolet has been measured and discussed by King and Moule [13]. Our remeasured  $S_1 \leftarrow S_0$  spectrum shown in fig. 1 agrees well with the previous one except for a slightly different intensity pattern. Due to the coexistence of trans- and cis-HONO at room temperature ( $p_{\text{trans}}: p_{\text{cis}}=2.5$ ), the spectrum is a superposition of two similar, but displaced spectra.



Fig. 1. Gas-phase absorption spectrum  $S_1(n\pi^*) \leftarrow S_0$  of HONO at room temperature. The spectrum is a superposition of trans-HONO (A, B, ...; a, b, ...) and cis-HONO (A", B", ...) and was obtained from an initial mixture of NO<sub>2</sub>:NO:H<sub>2</sub>O = 17:100:17 at a total pressure of 100 Torr. Based on the ab initio calculation the position of the O-O band of cis-HONO (A" or A<sub>0</sub>") cannot be established. Notation according to ref. [13].

The  $S_1 \leftarrow S_0$  transition energy for trans- and cis-HONO was calculated using the CI method with inclusion of the Davidson correction. For the more stable trans form a transition energy of 27980 cm<sup>-1</sup> (357.4 nm) was found, which is in excellent agreement with the maximum of the measured transition at 28200 cm<sup>-1</sup> (354.5 nm). The corresponding cis form transition is calculated to be at 28870 cm<sup>-1</sup> (346.4 nm), i.e. about 900 cm<sup>-1</sup> to the blue of trans-HONO.

The calculations support the suggestion by King and Moule [13] that the blue-shifted A", B", C", ... progression is due to the N=O stretching mode of the cis conformer. Subtraction of these progressions results in a spectrum which consists of only two progressions A, B, C, ... and a, b, c, .... This new spectrum is – apart from the band width – very similar to the theoretical trans-HONO spectrum based on the two-dimensional PES( $R_{O-N}$ ,  $r_{N=O}$ ) [3] which is displayed in the insert of fig. 1. It shows two progressions, namely the dominant progression due to the N=O stretching mode ( $n^*=0$ , 1, 2, ...) with  $\tilde{\nu}_{N=O} = 1150$  cm<sup>-1</sup> and the much less intensive O-N stretch progression ( $m^*=1$ ,  $n^*=0$ , 1, 2, ...) with  $\tilde{\nu}_{O-N} = 830$  cm<sup>-1</sup>.

The relative intensities and the vibrational frequencies of the experimental spectrum, i.e.  $\hat{\nu}(A, B, ...) \approx 1100 \text{ cm}^{-1}$  and  $\hat{\nu}(a, b, ...) \approx 820 \text{ cm}^{-1}$ , agree very well with the theoretical predictions allowing us to conclude that the trans-HONO spectrum can be well reproduced on the basis of the two-dimensional



Fig. 2. Potential energy surface of trans-HONO in the  $S_1$  state as a function of the N=O and O-N bond lengths. The ab initio calculation was performed with the MCSCF method.

PES  $(R_{O-N}, R_{N-O})$  shown in fig. 2. The shallow potential well characterizing this PES supports quasibound states that are described by the quantum numbers  $n^*$  and  $m^*$ , which correspond to those of

Table 1

Optimized geometries (bond lengths in Å, angles in deg) of cis- and trans-HONO in the  $S_0$  and  $S_1$  state using different methods of calculation

Conformation	Method	O-N	N <b>-</b> O	O-H	ONO	NOH	$\frac{\Delta E(\text{cis-trans})}{(\text{cm}^{-1})}$
trans (S <sub>0</sub> )	CISD	1.40	1.19	0.97	110.7	102.6	-60
cis (S <sub>0</sub> )	CISD	1.37	1.20	0.98	112.8	105.2	
trans $(S_0)$	CEPA-1	1.43	1 <b>.19</b>	0.97	110.5	101.7	30
cis $(S_0)$	CEPA-1	1.39	1.20	0.98	112.7	104.6	
trans $(S_0)$	exp. <sup>a)</sup>	1. <b>44</b>	1.17	0.96	110.6	102.1	180±90 <sup>b)</sup>
cis $(S_0)$	exp. <sup>a)</sup>	1.40	1.19	0 <b>.99</b>	11 <b>3.6</b>	104.0	
trans	MCSCF	1.34	1.35	0.95	104.5	105.1	

<sup>\*)</sup> Ref. [14]. <sup>b)</sup> Ref. [15].

the N=O and O-N stretching modes, respectively [3].

The calculated and the experimental geometries of trans- and cis-HONO are given in table 1. CISD and

CEPA-1 methods provide the cis and trans geometries in very good agreement with the experiment [14,15]. Furthermore, the comparison of the trans geometry in the  $S_0$  and  $S_1$  state confirms the ex-



Fig. 3. Contour plots of the ab initio S<sub>1</sub> potential energy surfaces of trans-HONO. (a) PES as a function of the coordinates  $R_{N-O}$  and  $R_{O-N}$ . (b) PES as a function of  $R_{O-H}$  and  $R_{O-N}$  with  $R_{N-O}$  fixed at 2.6  $a_0$  as indicated in the plot on the top. (c) PES as a function of  $R_{O-H}$  and  $R_{O-N}$  with  $R_{N-O}$  fixed at 2.21  $a_0$ . The crosses mark the ground state equilibrium positions; the energy spacing is 0.136 eV.

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Fig. 3. (continued).

pected geometry change upon a  $n\pi^*$  transition [13]. Thus, the N=O bond is extended by 0.18 Å (difference between experimental and calculated value) and the O-N bond is shortened by 0.10 Å. This fact is reflected in the measured vibrational frequencies, which are  $\tilde{\nu}_{N-O}^{"} = 1698$  and  $\tilde{\nu}_{O-N}^{"} = 793$  cm<sup>-1</sup> in the ground state [13,16] and  $\tilde{\nu}_{N-O}^{'} = 1100$  and  $\tilde{\nu}_{O-N}^{'} \approx 820$  cm<sup>-1</sup> in the S<sub>1</sub> state, respectively.

Table 1 lists also the calculated and experimental energy difference  $\Delta E$  of the cis and trans forms. Although the small  $\Delta E$ (cis-trans) value of merely  $180 \pm 90 \text{ cm}^{-1}$  [15] lies outside the accuracy of such calculations, the results clearly indicate very similar energies of cis- and trans-HONO in the ground state. The energy barrier for isomerization as well as structural parameters of ground state HONO have recently been calculated by Turner [17] and Darsey and Thompson [18].

### 3.2. Potential energy surface and the NO channel

The  $S_1(n\pi^*) \leftarrow S_0$  absorption of HONO is localized on the N=O group. Therefore, the two-dimensional PES involving the coordinates  $R_{N=O}$  and  $R_{O-N}$  displayed in fig. 2 contains the information to interpret the main features of the absorption spectrum. The contour plot of this PES (fig. 3, top) exhibits a shallow well in the excitation region which introduces a small barrier along the reaction coordinate, and a curved minimum energy path that reflects the strong interaction between the N=O and O-N motions during the S<sub>1</sub> dissociation process. A brief inspection of this contour plot permits prediction of the absorption spectrum. The equilibrium ground state geometry of the N=O and N-O bond lengths is indicated by a cross and represents the center of the Franck-Condon (FC) transition region. With respect to the N=O coordinate the  $S_1$  PES is displaced relative to the S<sub>0</sub> PES and also distorted giving rise to a progression of the N=O stretching vibration in the absorption spectrum which reaches the maximum with the third member of the progression (cf. fig. 1). For the case of a classical trajectory starting from the FC region, this PES permits a path which is, according to the steepest descent, initially directed along the N=O coordinate. Under the influence of the potential, determined by the shallow well, this motion is gradually rotated into a motion directed along the N-O (reaction) coordinate with a strong N=O oscillation. These features lead to the diffuseness of the vibronic absorption bands of the N=O stretch (fwhm  $\approx 130 \text{ cm}^{-1}$ ) and to the strong vibrational excitation of the NO fragment. The experimentally observed, high rotational excitation of the fragment NO ( $\langle J \rangle \approx 30$ ) is also well reproduced by the S<sub>1</sub> PES if the ab initio calculations are extended to include a third dimension, i.e. the angle ONO [19].

# 3.3. The potential energy surface and the OH channel

The PES with variation of the O-H and O-N bond lengths was calculated by treating the N-O distance as a parameter and leaving the rest of the coordinates fixed at the ground state geometry. Figs. 3b and 3c exhibit contour plots for  $R_{N=0} = 2.60$  and 2.21  $a_0$ , which correspond approximately to the equilibrium bond lengths in the  $S_1$  and  $S_0$  states, respectively (fig. 3a). The center of the FC region is indicated by a cross and shows that the O-H bond length is essentially unchanged on the  $S_1$  surface (see also table 1). in other words, the potential curve along the O-H coordinate is not displaced. Even in a small molecule like HONO the  $n\pi^*$  excitation is thus highly localized on the NO group and does not appreciably influence the rest of the molecular geometry. Given the fact that the OH bond length in the parent molecule (R=0.96 Å [14]) is unchanged upon excitation, and is also not much changed when going to the free OH radical (R = 0.97 Å [20]) one would expect a straight minimum energy path along the O-N reaction coordinate, i.e. an almost constant O-H bond length during the O-N bond breaking process. This is confirmed by the calculations. Furthermore, changes of the  $R_{N=0}$  coordinate (cf. figs. 3b and 3c) as well as the ONO angle, have practically no influence on the O-H bond distance. The O-H coordinate acts like a spectator in the dissociation process of eq. (1) and as a consequence the emerging O-H fragment will not be vibrationally excited. This result agrees with the experiment which has shown the nascent OH product to be vibrationally (and rotationally) cold [1].

As in the case of methyl nitrite [4,5], the experimental results in combination with theoretical studies permit us to elucidate the microscopic decay mechanism of the predissociation process of HONO.

In order to predict not only the quantitative vibrational state distribution in the NO [3] and OH fragments but also the rotational state distribution, we are in the process of extending our calculations to include the HON and ONO angle as additional coordinates for the  $S_1$  PES.

# Acknowledgement

Support of this work by the Schweizerischer Nationalfonds is gratefully acknowledged. We thank Rolf Pfister for recording the absorption spectrum of HONO and Drs. Marco Nonella and Reinhard Schinke (Göttingen) for valuable discussions. We also thank Professor R.N. Dixon and Dr. H. Rieley (Bristol) for communicating their results on HONO prior to publication. Computer time has been provided by the Computing Center of the University of Zurich.

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