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THE BINDING ENERGY BETWEEN NO AND NO⁺

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ABSTRACT

The photoionization efficiency curve of the nitric oxide dimer (NO)₂ was obtained in the wavelength range from 1420Å to 1230Å (8.731 eV - 10.080 eV). The ionization potential of (NO)₂ was found to be 8.752 eV ± 0.008 eV. From the structure of the photoion yield curve of (NO)₂, NO(²Π, v''=0)-NO⁺(X¹Σ⁺, v') is found to be bound when NO⁺(X¹Σ⁺) is in the v'=0 or 1 vibrational state. From this and the dissociation energy of (NO)₂ (0.069 eV ± 0.003 eV) obtained by Billingsley and Callear, the dissociation energy of NO(²Π, v''=0)-NO⁺(X¹Σ⁺, v'=0) is deduced to be 0.573 eV ± 0.008 eV.

Introduction

The important role played by the nitric oxide dimer in many atomic and molecular processes has been recognized recently. For example, the chemiluminous reaction $(\text{NO})_n + \text{O} \rightarrow \text{NO}_2^* + (\text{NO})_{n-1}$ is found to be several orders of magnitude faster than the three body reaction of $\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2^* + \text{M}$.¹⁻³ Both the rapid vibrational relaxation of nitric oxide⁴ and anomalous thermodynamic properties of gaseous nitric oxide at low temperatures⁵⁻⁸ are attributed to the existence of $(\text{NO})_2$. The nitric oxide dimer $(\text{NO})_2$ in the gas phase has been directly observed by mass spectrometric sampling of an expanding NO jet⁹⁻¹⁰ using an electron bombardment type ionizer. From studies of the ultraviolet spectrum¹¹⁻¹² and infra-red transitions of the dimer in the gas phase,¹³ the heat of formation of the dimer has been estimated to be 2.45 kcal/mol. The structure of the nitric oxide dimer $(\text{NO})_2$ has been determined in the gas phase by infrared measurements,¹³ and in the solid state by x-ray crystallography.¹⁴⁻¹⁵ It is found that $(\text{NO})_2$ has a nearly rectangular cis configuration. In this work we report the first photoionization study of $(\text{NO})_2$. One of the main reasons for this study was to determine the binding energy between NO and NO^+ . If the ionization mechanism of $(\text{NO})_2$ is such that only one of the NO molecules in the dimer is being excited to the different vibrational states of $\text{NO}^+(\chi^1\Sigma^+)$, we would expect to see the same step-function behavior that is observed in the photoionization efficiency curve of NO alone. Furthermore, since the intermolecular energy transfer in the $\text{NO}-\text{NO}^+(\chi^1\Sigma^+v')$ complex is expected to be faster than the ion

transit time to the detector ($\sim 10^{-6}$ sec), if the energy of a certain vibrational level of $\text{NO}^+(\text{}^1\Sigma^+)$ is greater than the binding energy of NO-NO^+ , the complex will no longer be stable. Thus the number of steps observed in the photoionization efficiency curve will be related to the binding energy of $\text{NO-NO}^+(\text{}^1\Sigma^+)$. It is with this expectation that the photoionization study of $(\text{NO})_2$ has been carried out.

Experimental

The experimental apparatus is essentially the same as that described previously.¹⁶ Modifications were made such that the system can now be operated automatically.¹⁷ A stepping motor was installed in the McPherson 225 one meter monochromator. When the machine was operated in the automatic mode, the ion counters and the photon counter counted for a preset time at a certain wavelength and then the signals were printed out by a printer. Immediately after the printing, the stepping motor advanced upward or downward by a preset number of steps which corresponded to a certain increment of wavelength, and the scalers were reset and restarted simultaneously. The hydrogen many-line pseudo-continuum was used as the light source. The grating used was coated with MgF_2 and has 1200 lines/m.m. With the 300μ entrance and exit slits used in this experiment, the resolution was about $2.49\text{\AA}$ (i.e. ~ 16 meV at $1400\text{\AA}$). The nitric oxide used in this experiment was C.P. grade (99% minimum in purity) obtained from Matheson without further purification. A nozzle 0.127 mm in diameter was used. The photo-

ionization efficiency curve of $(\text{NO})_2$ was obtained with a nozzle stagnation pressure of 600 torr. The monochromator was scanned automatically at $1\text{\AA}$ intervals, and at each wavelength, the scalers were set to count for 300 sec. The counting rates varied from about 0.5 count/sec to 5 counts/sec. Wavelength calibration was accomplished by using the known emission lines of the hydrogen atom and molecule. The photon signal has been corrected for the background of stray photons from the monochromator.

Results and Discussion

The percentage of concentration of nitric oxide dimer versus nozzle stagnation pressure of nitric oxide at room temperature was obtained at $1215.7\text{\AA}$ (Lyman α). The results shown in Fig. 1 are calculated with the assumption that the photoionization cross section of $(\text{NO})_2$ is twice that of NO. It has been shown that when a gas is adiabatically expanded from a high pressure gas reservoir into a vacuum, association of the molecules occurs as a first step in the condensation process.¹⁸⁻¹⁹ Due to adiabatic cooling, the gas jet after expansion consists of a higher percentage of dimer as compared to the percentage before expansion. For a given gas, the degree of cooling through the expansion depends strongly on the parameter $P_0 \cdot D_0$, where P_0 is the nozzle stagnation pressure and D_0 is the diameter of the nozzle. It is seen that the concentration of the $(\text{NO})_2$ dimer relative to the monomer, NO, rises with increasing pressure. No attempt has been made to analyze the dimer formation in

the expanding gas beam of NO. However, it was found that with the present beam production arrangement, the concentration of $(\text{NO})_2$ is approximately proportional to P_0^2 .

The photoion yield spectrum of $(\text{NO})_2$ obtained is shown in Fig. 2. The photoionization efficiency curve of NO is also plotted for comparison. The ionization potential of $(\text{NO})_2$ obtained in this work is equal to $8.752 \text{ eV} \pm 0.008 \text{ eV}$, which is $0.504 \text{ eV} \pm 0.008 \text{ eV}$ lower than the I.P. of the NO molecule¹⁶ ($9.256 \text{ eV} \pm 0.003 \text{ eV}$). The standard deviation of the photoionization efficiency at several points is shown in Fig. 2. Due to the small counting rate of $(\text{NO})_2^+$, the average standard deviation of this spectrum is as high as 15-20%. This prevents us from analyzing the fine structure of the spectrum.

The photoionization efficiency curve of NO has been found to follow predominately a step-function behavior which corresponds to direct ionization of NO ($v''=0$) to NO^+ ($X^1\Sigma^+$, $v'=0,1,2,3,4$ etc). Although the stability of $(\text{NO})_2$ is attributed to a weak "chemical bond" which arises from electron pairing between two ($^2\Pi$) NO molecules, the coupling between the two interacting NO molecules will still be weak. The unpaired electron will mainly be localized on each NO molecule. Thus when a photon comes in and knocks out an electron, the ionization process is expected to be similar to that of NO alone. The only difference is that the ionization potential of the $(\text{NO})_2$ will be shifted to lower energy due to the interaction of the ion with its partner NO molecule. However, in the photoion yield curve of $(\text{NO})_2$, only two steps are clearly resolved. They are separated by 0.290 eV , which is the vibrational quantum of the NO molecule.

In order to explain the observed features in the photoionization efficiency curve of $(\text{NO})_2$, schematic representations of the potential energy curves for $(\text{NO})_2$ and $(\text{NO})_2^+$ are shown in Fig. 3. The quantities ϵ and ϵ^+ are the dissociation energies of NO-NO and NO-NO^+ , respectively. The ionization process of $(\text{NO})_2$ involves ejecting an antibonding electron which is associated with one of the NO molecules. This can result in the excitation of the stretching vibrational mode of NO^+ . The onset of the first step in the photoion yield curve (i.e. the I.P. of $(\text{NO})_2$) can be attributed to the ionization threshold of $(\text{NO})_2$ to form NO-NO^+ ($v=0$). The onset of the second step is then equal to the I.P. of $(\text{NO})_2$ to form NO-NO^+ ($v=1$). With this model, the nonexistence of the third step in the photoion yield curve implies that NO-NO^+ ($v=2$) has an energy larger than the ion-neutral bond energy. Intramolecular energy transfer is expected to be fast and the dimer dissociates in less than $\sim 10^{-6}$ sec (i.e. the estimated flight time from the ionizing region to the entrance of the quadrupole mass spectrometer). Thus we have

The charge exchange cross section between the neutral NO molecule and the NO^+ molecular ion is expected to be large. This does not change any of the argument presented above. The fact that NO-NO^+ ($v=1$) is bound but NO-NO^+ ($v=2$) is not, permits a measurement of the well depth of (NO-NO^+) . The minimum well depth for the NO and NO^+ interaction is $0.290 \text{ eV} \pm 0.008 \text{ eV}$ (ϵ_{min}^+) and the maximum is estimated to be $0.580 \text{ eV} \pm 0.008 \text{ eV}$ (ϵ_{max}^+), which correspond to the vibrational

energies of NO^+ ($v=1$) and NO^+ ($v=2$), respectively. From Fig. 3, the following relation can be derived:

$$\epsilon^+ + \text{I.P.}((\text{NO})_2) = \text{I.P.}(\text{NO}) + \epsilon \quad (1)$$

Using ϵ_{max}^+ and substituting into equation (1), an upper bound for the dissociation energy of $(\text{NO})_2$ is found to be $0.076 \text{ eV} \pm 0.008 \text{ eV}$. On the other hand, with the value of $0.069 \text{ eV} \pm 0.004 \text{ eV}$ for the dissociation energy of $(\text{NO})_2$ as determined by Billingsley and Callear, we would obtain a value of $0.573 \text{ eV} \pm 0.008 \text{ eV}$ for the dissociation energy of $(\text{NO}-\text{NO}^+)$. This certainly lies within our estimates.

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FIGURES

- Fig. 1. Variation of concentration of nitric oxide dimer with nozzle stagnation pressure at room temperature as probed at Lyman α (1215.66Å). The dashed line is the best fit to the experimental points, and is given by % of $(\text{NO})_2 = (7.97 \times 10^{-4}) [P_0 \cdot D_0]^2$ where P_0 is the nozzle stagnation pressure in torr, and D_0 is the nozzle diameter (0.0127 cm).
- Fig. 2. Photoionization efficiency curve of $(\text{NO})_2$ in the wavelength range from 1230Å to 1425Å (10.080 eV - 8.700 eV).
- Fig. 3. Schematic representation of $\text{NO} + \text{NO}$ and $\text{NO} + \text{NO}^+$ potential energy curves. ϵ^+ and ϵ denote the dissociation energies of $(\text{NO})_2^+$ and $(\text{NO})_2$, respectively.

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Fig. 1

Fig. 2

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Fig. 3

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