Unlike reaction 1, which is endothermic, reaction 2 is exothermic by 0.45 eV. This small exothermicity is not, however, sufficient to lead to any electronically excited products, and we therefore assign reaction 2 as the exclusive pathway for photoenhanced dissociative attachment under these conditions.

Discussion

The electron configuration of the $A^2\Sigma^+$ state of NO is $2p\pi^4 3s\sigma$ and is described well as a Rydberg state of NO. The attachment of an electron to form the NO^- ion at energies near this state was investigated experimentally by Sanche and Schulz,[12] who measured the transmission of monochromatic electrons between 5 and 7.5 eV. These authors observed four sequences of resonances, each with energy spacings similar to the vibrational energy differences of NO^+ in its ground electronic state. By comparing the spacings and intensities of the electron transmission resonances with the vibrational energies and Franck–Condon factors of the ground state of NO^+, they assigned these resonances to four excited electronic states of the NO^- ion, each composed of two Rydberg electrons bound to the $^1\Sigma^+$ core of NO^+.

Later, Lefebvre-Brion confirmed this assignment theoretically. Using the stabilization method of Taylor,[13] Lefebvre-Brion calculated the energies of the states of NO^- corresponding to the resonances observed by Sanche and Schultz and attributed the four resonances to the $(Rs\sigma)^2\ {}^1\Sigma^+$, $(Rs\sigma)(Rp\pi)\ {}^3\Pi$, $(Rs\sigma)(Rp\sigma)\ {}^3\Sigma^+$, and $(Rp\pi)^2\ {}^3\Sigma^-$ states.[14] The electron affinity of the A state of NO with respect to these excited states of NO^- is 0.45, 0.07, 0.02, and −0.96 eV, respectively.

Among these states, the only state which can lead to dissociation to ground state N and O^- products is the $(Rs\sigma)(Rp\pi)\ {}^3\Pi$ state. Strictly speaking, this state does not correlate directly with the products we observe; it does, however, cross a repulsive state of the same symmetry which does correlate with those products (see Figure 1). On this basis, we assign the photoenhanced dissociative attachment as proceeding through predissociation of the quasi-bound $^3\Pi$ state of NO^-.

These results suggest that the population distribuion of electronic states of small molecules such as NO is extremely important in determining the chemical fate of such molecules in discharges. Low-temperature electrons are incapable of attaching to a molecule such as NO in its ground state; if the molecule is in its $A^2\Sigma^+$ state, however, the dissociative attachment cross section may be very large. We estimate, based on the observed ion currents, that the cross section for dissociative attachment to the $A^2\Sigma^+$ state of NO is at least a factor of 10 greater than for the maximum cross section for the ground state, which is 10^{-18} cm^2 at 8.1 eV.[15]

There are several other possible mechanisms for producing O^- which must be considered and eliminated before the above mechanism can be established. These include photodissociation of NO^-, collision of ground-state NO with fast electrons arising from superelastic collisions, and dissociative attachment of electrons to vibrationally excited NO. The first of these, photodissociation of NO^-, may be excluded immediately because the optical spectrum of O^- production is identical with that of neutral NO; furthermore, we observe no mass signal corresponding to NO^- ions. The second process would be represented by the reactions

$$NO^*(A^2\Sigma^+) + e(\text{slow}) \rightarrow NO(X^2\Pi) + e(\text{fast}) \qquad (3)$$

and

$$NO(X^2\Pi) + e(\text{fast}) \rightarrow O^-(^2P) + N(^2D) \qquad (4)$$

Because the fast electrons produced in reaction 3 would have energies far below the 7.42-eV threshold energy required for reaction 4, this process can also be ignored. The final process is represented by the equation

$$NO^*(X^2\Pi) + e \rightarrow O^-(^2P) + N(^4S) \qquad (5)$$

where $NO^*(X^2\Pi)$ designates some vibrationally excited level of the ground electronic state. Although reaction 5 has never been observed, it is difficult to discard this possibility out of hand, since no systematic studies have been performed of highly excited vibrational levels of NO. The vibrational levels populated by spontaneous emission are, however, relatively low lying because of the Franck–Condon factors involved, and collisional processes are expected to be unimportant in our experiment because of the low pressures involved. We therefore believe reaction 2 is the exclusive mechanism for producing O^- ions in this experiment.

This technique offers a potential method for studying the dissociative attachment of electrons to small molecules in rovibronically selected states. Such studies are, in principle, capable of probing the dissociative potential functions of the negative ion. Inasmuch as there are few experimental techniques for exploring these excited potential curves, the information gained would be unique. We have detected no rotational effect on the cross section for dissociative attachment; however, our signal/noise ratio is such that only very coarse effects could be detected.

Finally, our experimental results indicate that autodetachment competes inefficiently with predissociation in determining the fate of the $(Rs\sigma)(Rp\pi)\ {}^3\Pi$ state of NO^-. This conclusion suggests in turn that photodissociation studies on the NO^- ion in the $A^3\Pi$–$X^3\Sigma^-$ system may yield spectra which are rotationally sharp.

Acknowledgment. This work was supported by the United States Army Research Office under Grant DAAL 03-88K-0070.

---

[12] Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1972**, *6*, 69.

[13] Hazi, A. U.; Taylor, H. S. *Phys. Rev. A* **1970**, *1*, 1109.

[14] Lefevre-Brion, H. *Chem. Phys. Lett.* **1973**, *19*, 456.

[15] Rapp, D.; Briglia, D. D. *J. Chem. Phys.* **1965**, *43*, 1480.

Absolute Orientation of Water Molecules at the Neat Water Surface

M. C. Goh, J. M. Hicks, K. Kemnitz, G. R. Pinto, K. Bhattacharyya, K. B. Eisenthal,*

Department of Chemistry, Columbia University, New York, New York 10027

and T. F. Heinz

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598 *(Received: July 8, 1988)*

The technique of second harmonic generation is employed to infer the net orientation of water at the neat liquid surface by a measurement of the absolute phase of the surface nonlinear susceptibility. The temperature dependence of the second harmonic signal is measured in order to determine the dipole contribution to the total susceptibility.

We report studies on the orientation of water molecules at the water liquid/vapor interface. The issue we consider is the sense of direction of the water molecule at the interface, i.e., do the protons point, on the average, toward the vapor or the liquid. The technique we use, second harmonic generation, has the important feature of selectively probing the interface between centrosym-

0022-3654/88/2092-5074$01.50/0

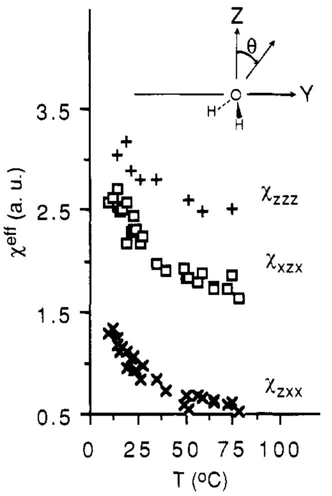

Figure 1. The effective susceptibility with varying temperature: (+) χ_{ZZZ}^{eff}, (×) χ_{ZXX}^{eff}, (○) χ_{XZX}^{eff}. The surface is on the X–Y plane.

metric media in the dipole approximation.[1] To obtain the absolute orientation of water molecules at the interface, we use a procedure[2] developed for measuring the absolute phase of the elements of the surface nonlinear susceptibility tensor χ. In the dipole approximation, the absolute orientation of molecules at an interface can be obtained from such phase measurements.[2]

For the case of water, however, there is a difficulty that must be addressed before this approach can be used. Since its dipole susceptibility is small, contributions from bulk and surface quadrupole terms to the total susceptibility χ^{eff} must be considered. Indeed our measurements of the relative magnitudes of two of the susceptibility tensor elements, χ_{XZX} and χ_{ZXX}, show that quadrupole contributions cannot be neglected. In the limit of being far from a molecular transition, the Kleinmann symmetry rule[3] requires that these elements be equal; we find at 20 °C that χ_{XZX} is about 2.3 times larger than χ_{ZXX}, indicating a significant quadrupole contribution.

To separate the dipole and quadrupole susceptibility contributions we note that the dipolar part is strongly dependent on the absolute orientation of molecules, i.e., up vs down, whereas the quadrupolar contribution is only weakly dependent on such. Since two molecules having opposite orientation would mutually cancel their contribution to χ^{dipole}, randomization of molecular orientations with increasing temperature would eventually reduce it to zero. We thus expect a much stronger temperature dependence of χ^{dipole} than $\chi^{\text{quadrupole}}$, whose isotropic part would remain even at temperatures where the molecular orientations are random. We therefore seek to distinguish between these two by studying the temperature dependence of the second harmonic (SH) signal.

Measurements were carried out in a sealed container from 9 to 80 °C with the temperature held constant to 0.2 °C by a Neslab circulator. The experimental apparatus has been previously described.[4] By choosing the input polarization and measuring the appropriately polarized SH signal, we obtain χ_{XZX}^{eff}, χ_{ZXX}^{eff}, and χ_{ZZZ}^{eff}. The latter requires values for the other two for its determination. The results are summarized in Figure 1. Both χ_{XZX}^{eff} and χ_{ZXX}^{eff} show an initial rapid decay that flattens out at higher temperatures. In addition, we note that the magnitudes of their rapidly decaying components are approximately equal. We interpret this rapid decay at low temperatures as the dipole part, χ^{dipole}, which is consistent with the expected decrease in alignment with increasing temperature. Their roughly equal values further support this assignment as dipole in origin, in accord with the Kleinmann symmetry rule.[3] As seen in Figure 1, χ_{ZZZ}^{eff} shows a similar, although not identical, temperature dependence to that of χ_{ZXX}^{eff} and χ_{XZX}^{eff}. The monotonic decay of χ^{eff} indicates that the phase of the dipole and quadrupole contributions are the same; otherwise, χ^{eff} would increase with temperature as the dipole part decreases.

A separate measurement determined the phase of χ_{XZX}^{eff} to be 180° with respect to the pump fields. By finding the SH polarization at various input polarizations, we deduce that χ_{ZXX}^{eff} and χ_{ZZZ}^{eff} have the same phase as χ_{XZX}^{eff}. We can then use the following relationship between the macroscopic dipolar susceptibility and the molecular hyperpolarizability elements to obtain the absolute orientation

$$\chi_{ZZZ}^{\text{dipole}} + 2\chi_{ZXX}^{\text{dipole}} = N_S(\alpha + \beta)\langle\cos\theta\rangle \qquad (1)$$

where N_S is the number of surface molecules and θ is the angle between the permanent water dipole and the laboratory normal. This equation can be derived with the minor approximation of neglecting the much smaller out-of-plane hyperpolarizability components compared with the in-plane hyperpolarizabilities α and β. As seen in (1), information about the signs of the χ's and $(\alpha + \beta)$ is required to determine the net orientation of the water dipole. While our data for the phase refers to χ^{eff}, we have concluded that both terms in χ^{eff} have the same phase in each case: thus all χ^{dipole} are negative. The left-hand side of (1) is thus negative. In order to determine if $\langle\cos\theta\rangle$ is positive, which corresponds to the protons pointing toward the vapor, or the reverse, we need information on the sign of $(\alpha + \beta)$. Theoretical calculations on the isolated water molecule[5] yield a negative value for $(\alpha + \beta)$; this leads to a positive $\langle\cos\theta\rangle$; i.e., protons are up. However, measurements of dc-induced second harmonic generation (SHG) in bulk water[6] have been interpreted to give a positive $(\alpha + \beta)$; this coupled with our results give a negative $\langle\cos\theta\rangle$. It is plausible to expect that $(\alpha + \beta)$ obtained for the bulk liquid rather than for the isolated molecules better corresponds to the molecular hyperpolarizability in the interface of an associated liquid. Our experimental results then imply that the protons are down, which is in accord with a number of theoretical studies.[7-13] It is of interest that one of these, a recent molecular dynamics simulation of the water interface,[13] showed the protons predominantly pointing up on the vapor side and down on the liquid side. This model would also be consistent with our SHG phase determination for any relative density of molecules on the vapor and liquid side, provided that the nonlinear response of the isolated molecule is used for the vapor side, and the bulk liquid measurement is applied to the liquid side. It should be recognized that a definitive conclusion requires further research on the molecular hyperpolarizabilities in the environment of an interface.

Acknowledgment. We gratefully acknowledge the National Science Foundation, the Air Force Office of Scientific Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support.

---

(1) Shen, Y. R. *Principles of Nonlinear Optics*; Wiley: New York, 1984; Chapter 25. Shen, Y. R. *J. Vacuum Sci. Technol.* **1985**, B3, 1464.

(2) Kemnitz, K.; Bhattacharyya, K.; Hicks, J. M.; Pinto, G. R.; Eisenthal, K. B.; Heinz, T. F. *Chem. Phys. Lett.* **1986**, 131, 285.

(3) Kleinmann, D. A. *Phys. Rev.*, **1962**, *126*, 1977.

(4) Hicks, J. M.; Kemnitz, K.; Eisenthal, K. B.; Heinz, T. F. *J. Phys. Chem.* **1986**, *90*, 560.

(5) Svendsen, E. N.; Willand, C. S.; Albrecht, A. C. *J. Chem. Phys.* **1985**, *83*, 5760. Purvis, G. D.; Bartlett, R. J. *Phys. Rev. A* **1981**, *23*, 1594.

(6) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1976**, *65*, 2429.

(7) Weyl, W. A. *J. Colloid Sci.* **1951**, *6*, 389.

(8) Stillinger, F. H.; Ben-Naim, A. *J. Chem. Phys.* **1967**, *47*, 4431.

(9) Fletcher, N. H. *Philos. Mag.* **1968**, *18*, 1287.

(10) Townsend, R. M.; Gryko, J.; Rice, S. A. *J. Chem. Phys.* **1985**, *82*, 4391.

(11) Croxton, C. A. *Physica A (Amsterdam)* **1981**, *106A*, 239.

(12) Wilson, M. A.; Pohorile, A.; Pratt, L. R. *J. Phys. Chem.* **1987**, *91*, 4873.

(13) Matsumoto, M.; Kataoka, Y. *J. Chem. Phys.* **1988**, *88*, 3233.