9180 J. Phys. Chem. A **2000,** *104,* 9180−9183

The $\tilde{A} \leftarrow \tilde{X}$ (1 + 1) Resonance-Enhanced Multiphoton Ionization Spectrum of the $NO{\cdot}C_2H_6$ and $NO{\cdot}(C_2H_6)_2$ Complexes

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Received: May 22, 2000; In Final Form: July 24, 2000

The $\tilde{A} \leftarrow \tilde{X}$ transitions of $NO{\cdot}C_2H_6$ and $NO{\cdot}(C_2H_6)_2$ have been recorded using (1 + 1) resonance-enhanced multiphoton ionization spectroscopy. The $NO{\cdot}C_2H_6$ origin is determined to be 44050 ± 15 cm^{-1}, and the dissociation energy, D_0', of the $\tilde{A}$ state is measured to be 340 ± 20 cm^{-1}. The latter values allow the dissociation energy of the $\tilde{X}$ state, D_0'', to be determined as 190 ± 20 cm^{-1}. In addition, estimates of the dissociation energies for the processes $NO{\cdot}(C_2H_6)_2 \rightarrow NO{\cdot}C_2H_6 + C_2H_6$ and $NO{\cdot}(C_2H_6)_2 \rightarrow NO + 2C_2H_6$ in the $\tilde{X}$ and $\tilde{A}$ states are obtained; the $\tilde{A}$ state is found to be dissociative along the $NO{\cdot}C_2H_6{\cdots}C_2H_6$ coordinate. Comparison of the $NO{\cdot}C_2H_6$ $\tilde{A} \leftarrow \tilde{X}$ spectrum with that of $NO{\cdot}CH_4$ is made.

I. Introduction

In recent years, the electronic spectroscopic study of van der Waals complexes containing open-shell diatoms interacting with a closed-shell atom has attracted some attention,[1] with the majority of studies concentrating on the lowest energy (allowed) transition. Interestingly, many of the detailed studies have focused on OH- and SH-containing complexes,[2−4] whereas complexes containing the stable NO radical have only recently attracted some notice. Much attention has been focused on the $\tilde{A}$ state of Rg·NO complexes (Rg = rare gas),[5−9] but there has also been significant progress in the understanding of the spectra of the higher ($\tilde{C}$, $\tilde{D}$, and $\tilde{E}$) electronic states.[10−13] Studies have also been performed on complexes containing a closed-shell molecule interacting with an open-shell diatomic partner, with those on $H_2{\cdot}OH$ being the most detailed.[14] Again, studies on NO-containing complexes have lagged behind, but there have been reports of the $\tilde{A} \leftarrow \tilde{X}$ transition of $NO{\cdot}CH_4$ (and $NO{\cdot}CD_4$)[15] and $NO{\cdot}N_2$ (ref 16). In passing, we note that the NO·HF dimer has been observed by both infrared[17] and microwave spectroscopy.[18]

In the present work, we have recorded the spectrum of the NO·Et (Et = ethane) complex for the first time, and also obtained a spectrum for $NO{\cdot}Et_2$.

II. Experiment

The experimental apparatus is a standard two-chamber resonance-enhanced multiphoton ionization (REMPI) apparatus, and so will only be described briefly below.

The NO·Et complexes are formed by a supersonic expansion of a mixture of NO and ethane, with argon as the carrier gas. The optimum mixture was found to be 4% NO and 12% ethane in 5 bar of Ar. The mixture is expanded through a pulsed nozzle (diameter 750 μm) into a vacuum chamber. This vacuum chamber is connected to a second (ionization) chamber, into which the expansion passes. It is there intersected with the output of a frequency-doubled dye laser, operating on Coumarin 450. The dye laser (Sirah, Cobra Stretch) is pumped by a XeCl excimer laser (Lumonics, PM 842). The output of the dye laser is frequency doubled in a BBO crystal, and the resulting UV (~1 mJ $pulse^{-1}$) is then steered and focused (f = 25 cm, slightly defocused) into the ionization chamber. The resolution of the frequency-doubled radiation is *ca.* 0.5 cm^{-1}.

The molecules and complexes are ionized by (1 + 1) REMPI. The resulting cations are extracted into a time-of-flight drift tube and detected using microchannel plates (MCPs). A mass spectrum is produced by observing the ion current on the MCPs as a function of drift time. The ion current is displayed and measured on a digital oscilloscope (LeCroy, LT342), and is simultaneously gated and averaged by a boxcar (SRS SR250). The signal from the boxcar is sent to a personal computer for analysis.

Calibration was performed against features in the cold NO A ← X REMPI spectrum.[19]

III. Results and Discussion

a. NO·Et. Optimum expansion conditions were obtained by recording cold Ar·NO spectra;[9] these were consistent with a rotational temperature of ~2 K. Within the mass spectra it was possible to observe NO, Ar·NO, NO·Et, and (more weakly) complexes of $NO_x{\cdot}(Et)_y$ (x, y >1) within the spectral range scanned (44000−44800 cm^{-1}).

Figure 1 shows the $\tilde{A} \leftarrow \tilde{X}$ (1 + 1) REMPI spectrum of NO·Et obtained by gating over the mass 60 amu signal corresponding to NO·Et cations. Note that, in principle, this mass also corresponds to that of the NO dimer, but in separate experiments where no ethane was present, the signal from this species was very small, and was approximately constant over the spectral range scanned. Consequently, we are confident that the signal in the mass 60 amu channel arises only from $NO{\cdot}Et^+$.

As seen in Figure 1 limited structure was obtained from the spectrum. This lack of detailed structure is in contrast to that observed for other complexes in our apparatus, where detailed rovibronic structure has been observed for Ar·NO,[9] and Kr·NO and Xe·NO.[8] Our recent experiments on these complexes, and on NO itself, indicate that our resolution is ~0.3 cm^{-1}, and that the complexes have a rotational temperature of ~2 K under

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10.1021/jp001858d CCC: $19.00

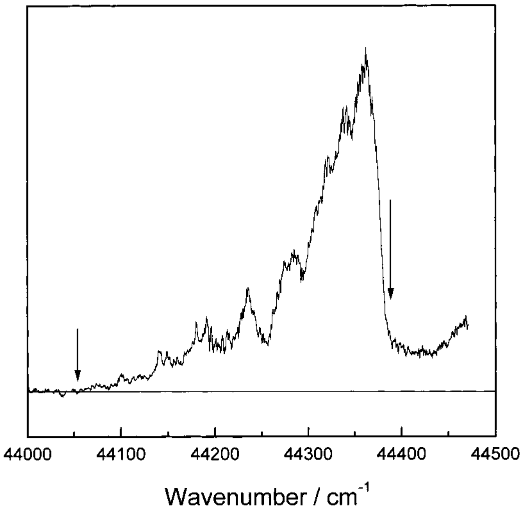

Figure 1. (1 + 1) REMPI spectrum of NO•Et recorded in the mass 60 amu channel. The rise in intensity at the end of the spectrum is due to $NO{\cdot}Et_2$ (see the text). The arrows mark the positions of the origin and dissociation limit.

optimal conditions. The apparent lack of structure here is thus probably due to unresolved rotational structure. Despite this, it is possible to derive information from this spectrum. First, the origin can be taken as the point where the signal starts its gradual rise from the baseline: this can be measured as 44050 ± 15 cm^{-1} (this weak onset is indicative of a significant geometry change between the $\tilde{X}$ and $\tilde{A}$ states). Second, the dissociation limit may be determined as the position of the sharp decline in intensity at high wavenumber, and was measured as 44390 ± 5 cm^{-1}. These two values give a dissociation energy of the $\tilde{A}$ state, D_0', as 340 ± 20 cm^{-1}. From this, and the known position of the $Q_{11}(0.5)$ line of NO at 44198.9 cm^{-1} (ref 19), D_0'' may be estimated from the equation

$$T_0(NO{\cdot}C_2H_6) - NO[Q_{11}(0.5)] = D_o'' - D_o'$$

This gives a value of $D_o'' \approx 190 \pm 20$ cm^{-1}.

Finally we note that there is some structure in the spectrum which may be seen to correspond to broad features separated by ~40 cm^{-1}. A probable assignment of these broad features is as a progression of the intermolecular stretch in the $\tilde{A}$ state. Within each of these bands there appears to be further structure (*vide infra*).

b. $NO{\cdot}Et_2$. It may be noticed that to the blue of the dissociation limit in the $NO{\cdot}C_2H_6$ REMPI spectrum (Figure 1) there is a rise in intensity. We investigated this by recording the spectrum to high wavenumber, while observing the mass spectrum. The latter indicated that there was a small, but significant, amount of $NO{\cdot}Et_2$ in the expansion, and so we recorded a REMPI spectrum gating over mass 90 amu, which is presented in Figure 2. (This could correspond to the NO trimer, but attempts to record structured spectra of this when ethane was absent were unsuccessful, and so we are confident the feature seen in Figure 1 is due only to $NO{\cdot}Et_2^+$.) As may be seen, this feature does have significant intensity to higher wavenumber similar to that observed in the NO•Et spectrum (the whole region recorded in the $NO{\cdot}Et^+$ mass channel is not shown). In fact the maximum intensity and high-wavenumber limit of the spectrum in the $NO{\cdot}Et_2^+$ mass channel match those in the $NO^+{\cdot}Et$ mass channel, but the intensity of this portion of the spectrum is stronger by 1 or 2 orders of magnitude in the $NO{\cdot}Et^+$ mass channel over that in the $NO{\cdot}Et_2^+$ mass channel. These facts, coupled with the lack of any structure, lead us to conclude that the $NO{\cdot}Et_2$ $\tilde{A}$ state is dissociative in nature along the NO•Et•••Et coordinate. The $NO{\cdot}Et_2^+$ ions arise from the competition between the (1 + 1) ionization and the dissociation at the one-photon level. The dissociative nature of the $\tilde{A}$ state of $NO{\cdot}Et_2$ presumably arises from steric effects, where the second ethane has no site in which to interact with the NO, owing to the presence of the first ethane. Note that the relative intensities of the $NO^+{\cdot}Et$ and $NO^+{\cdot}Et_2$ peaks were very similar under a variety of mixing ratios, with the $NO^+{\cdot}Et$ intensity always dominating.

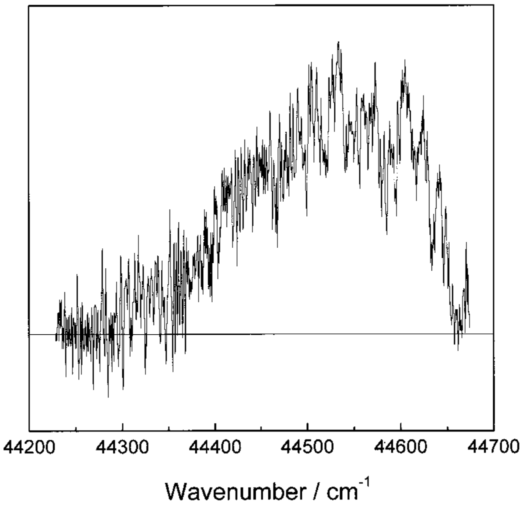

Figure 2. (1 + 1) REMPI spectrum of $NO{\cdot}Et_2$ recorded in the mass 90 amu channel.

The onset of the $NO{\cdot}Et_2$ spectrum is at 44300 ± 30 cm^{-1}, with the high-wavenumber limit at 44650 ± 10 cm^{-1}. Within experimental error, the difference between these two values is the same as the dissociation energy of $NO{\cdot}Et(\tilde{A})$. Thus, from this, and the conclusions of the previous paragraph, we conclude that the high-wavenumber limit is due to the photodissociation process: $NO{\cdot}Et_2(\tilde{X}) \rightarrow NO{\cdot}Et_2(\tilde{A}) \rightarrow NO(A) + Et + Et$. The cutoff in the $NO{\cdot}Et_2^+$ intensity at this point presumably arises from the opening up of the NO + 2Et continuum, further increasing the likelihood of dissociation over ionization.

These processes for $NO{\cdot}Et_2$ are illustrated in Figure 3, with the resulting energetics presented in Figure 4. The use of "*x*" for the dissociation energy for the process $NO{\cdot}Et_2(\tilde{A}) \rightarrow NO{\cdot}Et(\tilde{A}) + Et$ is because, although the evidence is that the $\tilde{A}$ state of $NO{\cdot}Et_2$ is dissociative along the NO•Et•••Et coordinate, there is an experimental error limit on the derivation of this value *via* an energy cycle.

c. Comparison of the $\tilde{A} \leftarrow \tilde{X}$ Spectrum of NO•Et with That of $NO{\cdot}CH_4$. As mentioned above, apart from $NO{\cdot}N_2$ (ref 16), $NO{\cdot}CH_4$ (ref 15) is the only other complex consisting of NO interacting with a molecule for which $\tilde{A} \leftarrow \tilde{X}$ spectra have been recorded. It is of interest to note also that the $NO{\cdot}CH_4$ complex has also been studied *via* the $\tilde{C}$ state by Miller,[20] where only broad structure was obtained—a result confirmed in ref 21. This result is in contrast to the more detailed structure that appears in the $\tilde{A} \leftarrow \tilde{X}$ spectrum[15] reported by Akiike *et al.* In that work, they interpreted the observed structure in terms of van der Waals vibrations, onto which was superimposed other structure assigned to internal rotation of the methane group. The relative intensities of the assigned internal rotation features changed somewhat with internal temperature, and more dramatically upon full deuteration. We have re-recorded spectra of the $\tilde{A} \leftarrow \tilde{X}$ transition of $NO{\cdot}CH_4$ and $NO{\cdot}CD_4$ under different conditions, and will present these results in a forthcoming

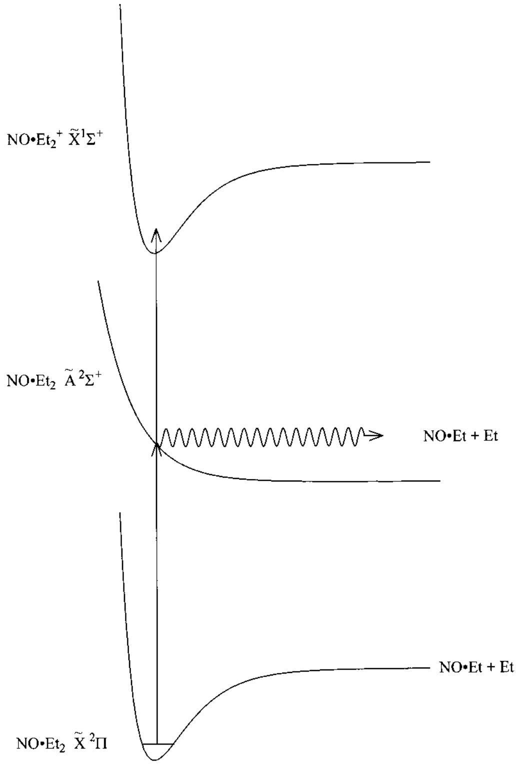

Figure 3. Schematic diagram showing the (1 + 1) REMPI process for NO•Et_2 in competition with the dissociation of the Ã state at the one-photon level.

paper,[22] but largely the appearance of the spectra matches those presented in ref 15.

The dissociation energies of the X̃ and Ã states of NO•CH_4 were derived as 121 and 216 cm^{-1}, respectively.[15] These may be compared to the corresponding values for NO•Et of 180 and 330 cm^{-1}. Thus, the NO•Et complex is more strongly bound in both states by ca. 50%. The static polarizabilities of methane and ethane are 2.59×10^{-24} and 4.47×10^{-24} cm^3 (ref 23), respectively, suggesting that the bonding in these species is not wholly electrostatic in origin—a conclusion that is consistent with our recent work on Kr•NO and Xe•NO (ref 8). It must be noted, of course, that the polarizability of C_2H_6 will be anisotropic, and the binding energy will be dependent upon orientation.

The X̃ state of NO has one unpaired electron in a 2pπ* orbital, and the Ã state is formed by excitation of this unpaired electron into a 3s orbital. Thus, in the Ã state, since the radial extent of the 3s electron is rather limited, the CH_4 and Et molecules must lie largely outside the 3s electron's orbit and experience Pauli repulsion with that electron, which explains the rather weak interaction. That the Ã state is more strongly bound than the X̃ state may be explained by the larger dipole of the Ã state of NO relative to the X̃ state [$\mu_x(NO) = 0.16$ D;[23] $\mu_A(NO) = 1.1$ D[24]], but this is tempered by the Pauli repulsion, leading overall to weak bonding. This weak bonding certainly rules out the possibility that the Ã state is a Rydberg electron interacting with a NO^+•Et core, and that essentially the Ã state is an ethane molecule interacting with the 3s Rydberg state of NO.

Recently we showed that for the Rg•NO^+ (Rg = He to Rn) complexes, the calculated binding energy scaled approximately with the polarizability,[25] ignoring orientational effects. The binding energy of the NO^+•CH_4 cation has been calculated to be $D_e^+ = 1910$ cm^{-1} ($D_0^+ = 1515$ cm^{-1}),[26] and so assuming proportionality with polarizability also to be applicable here, then D_e^+(NO^+•Et) may be estimated as 3300 cm^{-1}. This clearly supports the fact that there is little NO^+•Et character in the Ã state.

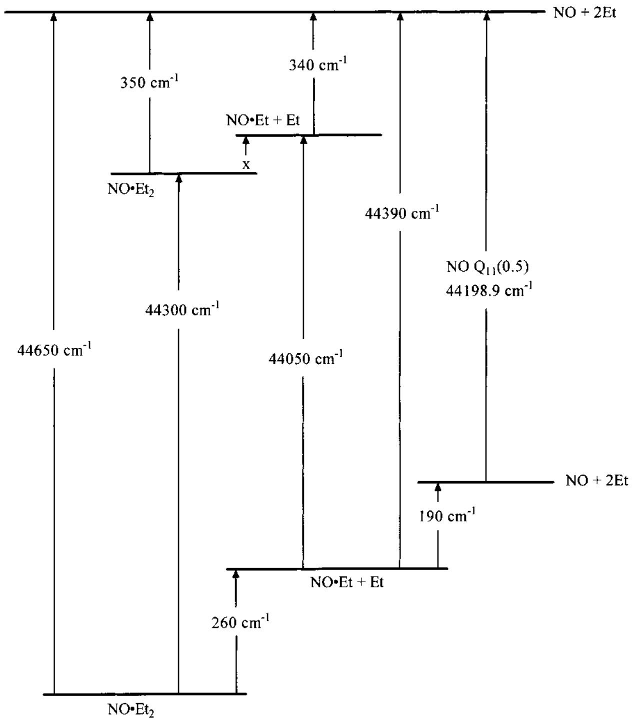

Figure 4. Summary of energetics for the NO•Et_2/NO•Et/NO system. "*x*" represents the dissociation energy of NO•Et_2(Ã) → NO•Et(Ã) + Et, which is zero within experimental error.

Finally, we note again that the structure observed in each of the bands in the REMPI spectrum of the Ã ← X̃ transition of NO•CH_4 was assigned in terms of internal rotation of the CH_4 group in ref 15, although this was questioned in ref 21, where it was suggested that the structure might also arise from rotation of the NO. These two possibilities will be discussed in a forthcoming paper on NO•CH_4.[22] On the basis of the present evidence, it is not possible to differentiate between these two possibilities for the structure observable within some of the 40 cm^{-1} bands in the NO•Et spectrum (Figure 1).

The NO•Et_2 spectrum shows no such structure, probably because of a combination of lifetime broadening and unresolved rotational structure.

IV. Conclusions

We have observed the Ã ← X̃ transition for NO•Et for the first time. From the spectrum we have been able to extract the dissociation energies of both the Ã and X̃ states. In addition, a progression of ~40 cm^{-1} was observed, which is tentatively assigned to the intermolecular stretch; within this progression, some partially resolved structure is seen, which may be due to motion of either the ethane or the NO moiety.

A second rise in the NO•Et^+ signal in the REMPI spectrum has been associated with the dissociation of the NO•Et_2 Ã state, and confirmed by the recording of a weak spectrum in the NO•Et_2^+ mass channel. The indications are that the Ã state of NO•Et_2 is dissociative along the NO•Et•••Et coordinate. The dissociation energies of NO•Et_2 in the X̃ state (NO•Et_2 → NO•Et + Et and NO•Et_2 → NO + 2Et) were also obtained.

Comparison of the NO•Et and NO•CH_4 Ã ← X̃ spectra was made. By assuming that the binding energies of the cations scale linearly with polarizability, it was possible to deduce that the Ã state of NO•Et contains very little cationic character.

Acknowledgment. We are grateful to the EPSRC, NERC, and Royal Society for funding. Dr. R. A. Jackson is thanked for the donation of ethane for the initial studies. TGW is grateful to the EPSRC for the award of an Advanced Fellowship.

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