Fluorescence Quenching by Oxygen. Lack of Evidence for the Complex Formation of Oxygen with 9-Cyanoanthracene and Anthracene in a Supersonic Free Jet

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To elucidate the efficient quenching process of the fluorescence of large organic molecules by molecular oxygen, the electronic absorption spectra were measured for 9-cyanoanthracene (9CNA) and anthracene (A) in a supersonic free jet with the seeding gas consisting of a mixture of the rare gases Ne, He, Ar, or Xe and molecular oxygen. No new spectral feature assignable to van der Waals complexes with oxygen was found, though the cooling efficiency of oxygen itself was quite good. Various sizes and shapes of the pulsed nozzle were tested and led to the same result. A coincidental overlap of the complex band with the band of the bare molecules was ruled out. The 9CNA−Ar$_n$ complexes with $n = 1-3$ were partially destroyed when oxygen was present in the mixture. At higher backing pressures, at which larger clusters were formed, the spectra observed suggest that oxygen can be accommodated within such a cluster and that the fluorescence of 9CNA was indeed quenched by the oxygen in the cluster. The lack of 9CNA−O_2 or A−O_2 complexes is discussed in comparison with the complex of 9CNA with iodine (I_2) and CO_2 formed in supersonic free jet.

Introduction

Molecular oxygen is a unique quencher of electronically excited states as it quenches both the singlet and triplet excited states of most organic molecules. Generally, the rate of reaction for the quenching by oxygen in solution is diffusion limited. Saltiel and Atwater discussed this quenching mechanism in a comprehensive review.[1] However, the true nature of the microscopic interaction between an organic molecule and molecular oxygen is not yet fully understood. The ground state interaction effected by van der Waals forces is very weak and better characterized as a contact state.[2] Hence, the elucidation of this contact ground state or van der Waals complex and its photodynamics would lead to a new insight into the true quenching mechanism. Unfortunately, the isolation of these contact state complexes has not been achieved yet for organic molecules, and the complexes have generally been analyzed from measurements of bulk properties. If these complexes could be studied without environmental perturbation, then they would be a good model for the reaction intermediate in the fluorescence quenching process by oxygen. Particularly, the parent molecules, which form complexes with oxygen in a supersonic free jet, would have their ligand in close vicinity. The rapid quenching process could be studied, therefore, as a function of the excess energy introduced into the parent molecule without the limitation by the translational diffusion of the oxygen molecules in the gas phase or in solution.

The technique of supersonic jet expansion[3] is a powerful tool for the study of electronic relaxation, electronic level structure, the intramolecular energy redistribution mechanisms, and, particularly, van der Waals complex formation. Laser-induced fluorescence excitation spectra (LIF) often provide important information, otherwise difficult to obtain, on fine structural and level-specific dynamical features of large molecules and van der Waals complexes. However, if the excited states are nonemitting or only very weakly emitting due to competing relaxation channels, then the LIF can provide no information, and emission lifetime data cannot be obtained. This is particularly true for the complexes with oxygen, because the emission lifetimes of these complexes will be very short due to instantaneous quenching by oxygen, and thus the very low fluorescence quantum yield makes it impossible to detect any fluorescence.

It is therefore straightforward to prove the formation of such nonemissive complexes by directly measuring the electronic absorption spectra in a supersonic free jet. This technique offers a unique possibility to study van der Waals complexes of oxygen and aromatic molecules in the isolated molecule limit without thermal congestion, and the role of vibrational excess energy of the complexes on the quenching mechanism could be clarified. The technique of directly measuring the electronic absorption spectra of nonvolatile solid compounds in a supersonic free jet has been developed by few groups,[4−10] because low sample densities and the resultant very low absorption have made these measurements difficult.

Whereas oxygen−rare gas, oxygen−diatomic, and oxygen dimer van der Waals complexes[11] were experimentally produced and investigated, there exists, to the best of our knowledge, no direct evidence for the complex formation in a supersonic free jet with larger molecules. Recent work on the aromatic hydrocarbon−oxygen interaction was performed by several groups. Ogilby's group[12,13] quantified the free energy of the benzene−oxygen complex formation as to be -5.0 ± 1.3 kJ mol^{-1} and demonstrated the existence of a charge-transfer (CT) state upon photoexcitation in the gas phase. Logunov and Rodgers[14] communicate an exciplex formation in solution between naphthalene and oxygen. Grover et al.[15] studied complexes of oxygen with benzene and hexafluorobenzene by photoionization and determined the dissociation energies to be 6.7 ± 1.3 and 8.8 ± 1.7 kJ mol^{-1}, respectively. The benzene−oxygen interaction potential was also accessed by theoretical calculation, and a dissociation energy of 5.20 kJ mol^{-1} was obtained.[16]

In the present work anthracene (A) and 9-cyanoanthracene (9CNA) were investigated for their ability to form oxygen van der Waals complexes. Both are fairly simple compounds and well-studied in supersonic free jet. Moreover, both are known to form heterocomplexes with a large variety of ligands. Among

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them are rare gases, water, carbon disulfide, ammonia, and ethanol.[17-20] The results acquired are discussed in relation to the formation of van der Waals complexes of 9CNA with CO_2 and I_2 as ligands.

Experimental Section

The experimental details of the measurement of the absorption and fluorescence excitation spectra in a supersonic jet are presented elsewhere in detail.[21] A brief summary and a description of some specific adaptations are given below.

Stainless steel nozzles of different sizes and shapes were used for the pulsed supersonic expansion: plain round types with diameters of 200 and 300 μm, a cone-shaped round type with a diameter of 200 μm, and a plain slit nozzle with the dimensions of 40 × 2000 μm. Nozzle open times were selected from 1 to 10 ms depending on the pulse repetition frequency and vacuum condition required. The temperature of the sample vessel was kept constant in the range 120−160 °C. To prevent the sample from condensing onto the nozzle, it was heated to a temperature higher than that of the sample by 5 °C. A 150 W dc Xe lamp was used as a light source for both the absorption and the fluorescence excitation measurements. Two lock-in amplifiers detected the corresponding signal modulated by the nozzle frequency. Thus, absorption and fluorescence excitation spectra could be measured simultaneously. The total fluorescence emission was measured for the excitation spectra. The lamp output power was recorded while scanning the wavelength, which allows the calculation of the absorbance of the sample.

For the absorption measurement, the noise of the system is mainly caused by the inherent noise of the monitoring light itself. In order to achieve a reasonable signal-to-noise ratio, it is therefore crucial to increase the throughput of the monochromator (MC-50N, Ritsu Oyo Kogaku Co., 50 cm, *f*/5.3). The spectral resolution was 0.9 Å at slit widths of 100 μm when equipped with a 2400 lines/mm grating.

The diatomic gases O_2, I_2, and N_2 and the triatomic gas CO_2, as well as the rare gases Ne, He, Ar, and Xe, were used as cooling and coordinating gases. The purity was as follows: Ne, 99.998%, He, 99.998%, Ar, 99.998%, Xe, 99.995% (all Sumitomo), CO_2, ≈98% (Iwatani), O_2, ≈98%, N_2, ≈98% (both Kyoto Iryoyo Sanso). Residual water molecules contained in the gases were removed by flowing the gas through a metal cylinder packed with silica gel. Solid I_2 (purity 99.9%, Wako) was put separately in a small vessel through which the seeding gas was flowed. The temperature of this dopant reservoir could be controlled in the range 0−60 °C. The vapor pressure of I_2 was evaluated using the Antoine equation. The flow of the cooling gas was controlled by a flow regulator (STEC, SEC 400), and the backing pressure was monitored by a pressure gauge (KH15, Nagano Keiki Seisakusho, Ltd.).

9-Cyanoanthracene (9CNA, Aldrich Chemical Co. Inc.) was purified by sublimation. Anthracene (A, Wako Pure Chemical Co., Ltd.) was of scintillation grade and used as received.

Results and Discussion

A. Spectroscopy of 9CNA Complexes with Rare Gases and Oxygen. van der Waals complexes of 9CNA with Ar and Xe could be easily detected by both absorption and fluorescence excitation spectra and assigned as reported previously[17,22] (see Figure 1). However, the bandwidths of the spectral bands are limited by the spectral resolution of the exciting light as given in the Experimental Section. The lack of a weak shoulder to the red of the electronic origin indicates sufficient cooling of the sample. The ratio of the absorption band intensity to that of the fluorescence excitation (not shown in the figure) is the same for the 0−0 band of the bare molecule and the complex bands, and therefore the relative fluorescence quantum yields of these complex bands must be unity. This is compatible with previous measurements of the fluorescence lifetime of the same complexes which revealed no shortening in the fluorescence lifetime as compared with that for the 0−0 band.[17,23,24] A higher backing pressure yielded more complexes with a larger number of coordinated atoms. The absorbance of the electronic origin band decreased to half of its value when the pressure of Ar was increased from 420 to 760 Torr, with a concomitant increase in the absorbance of the complexes. The high polarizability of Xe ($\alpha = 4.04 \times 10^{-24}$ cm^3)[25] led to very efficient complex formation even at a very low stagnation pressure of 100 Torr. When the stagnation pressure of Xe was increased to 200 Torr, the band associated with the 1:1 complex was greatly reduced, and complexes with higher coordination numbers were formed. No complexes were found at all for Ne or He in the low pressure range employed in this work,[26] and the cooling efficiency is considerably lower than that for Ar or Xe. Spectra obtained with Ne or He certainly have the advantage of no interfering complex bands, but the low cooling efficiency is a severe drawback in our system.

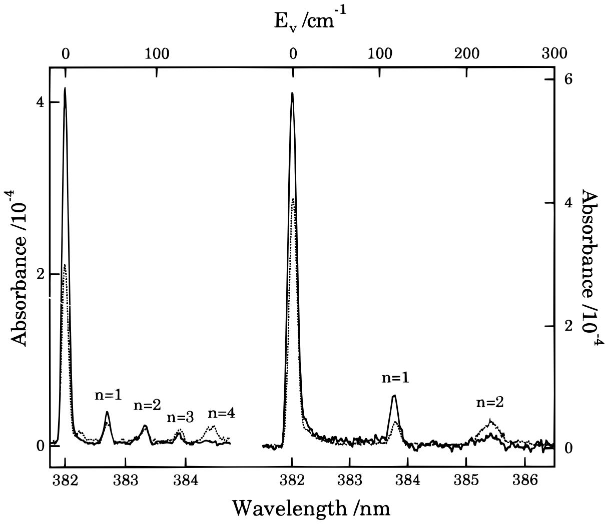

Figure 1. Absorption spectrum of 9CNA seeded in Ar (left) and Xe (right). The spectra are given for two different backing pressures of 420 and 760 Torr for Ar and 100 and 200 Torr for Xe, respectively. The nozzle was 300 μm in diameter and was kept at a temperature of 140 °C. The numbers given denote the number of coordinated atoms. The spectral shift for each complex agrees well with previous results.[17]

When oxygen was added to Ne, He, Ar, or Xe, no new spectral band assignable to a 9CNA−O_2 complex appeared in the spectra of Figure 1. Particularly, the absorption spectra did not alter upon adding oxygen, whereas the fluorescence excitation spectra might reveal no change due to the fluorescence quenching by oxygen. An increase of the partial pressure of oxygen did not lead to a decrease of the intensity of the electronic origin band. This is in sharp contrast to observations for many other ligands that form complexes.[19] At very low backing pressure the introduction of a small amount of oxygen improved the cooling efficiency to a certain extent, since the 0−0 band was sharpened and the red-shifted tail due to insufficient cooling was removed. The pressure of oxygen was varied in the range 5−500 Torr, with pressures of Ne, He, and Ar of 100−900 Torr and Xe of 80−400 Torr, although the total pressure could not exceed 1000 Torr.

Under normal experimental conditions the absorbance of the electronic origin of the bare molecule was on the order of (2−5) × 10^{-4}. Considering this, and a minimal detectable spectral feature having an absorbance of 5×10^{-6},[21] it can be concluded that a complex band with oxygen, if any exists, must have a minimum absorbance that is larger than 1% of the absorbance of the bare molecule at the 0−0 band. At higher pressures a rather short nozzle open time had to be chosen, which led to a low overall sensitivity. Therefore, for a new spectral feature to be detected at a total pressure of more than approximately 700 Torr, the absorbance of the band should be larger than about 3% of the absorbance of the electronic origin band. In order to increase the detection limit, the slit widths of the monochromator were increased to 200 μm. The 4-fold throughput resulted in a doubled signal-to-noise ratio, with a decrease of the spectral resolution to approximately 1.6 Å. However, as before, no new spectral feature assignable to 9CNA−O_2 van der Waals complexes could be detected.

The experiments were repeated for the different nozzle shapes and sizes with no success, although the cone-shaped type was found to enhance the complex formation with the rare gases, as is to be expected.[26] Furthermore, the distance between the nozzle and interrogating beam was varied from 5 to 15 mm. The wavelength range surveyed extended from 375 to 397 nm. It is very unlikely that the 9CNA−O_2 van der Waals complexes show such a large spectral red or blue shift that their electronic origin bands are located outside the wavelength range examined.

What else could cause the complete absence of any new spectral band when adding molecular oxygen? The bond energy between oxygen and 9CNA molecules might be coincidentally of the same magnitude in the ground and the excited state, whereas it is generally true for anthracene derivatives that the electronic origin of the first excited singlet state is, upon complexation, lowered to a greater extent than that in the ground state.[22] In the case of similar bond energies for the two electronic states, the oxygen complex band might be buried in the electronic origin band. This would lead to a decrease of the fluorescence intensity, when excited at the electronic origin band, due to the quenching of the excited state by a coordinated oxygen molecule, whereas the intensity of the band in the absorption would be unaltered. To verify this assumption, the ratio of the absorption to the fluorescence intensity for the electronic origin band was measured as a function of the partial pressure of oxygen. This ratio was found to be constant over the whole range of applied oxygen pressure, dismissing a coincidental superposition of the complex band on the 0−0 band of the bare molecule.

One interesting finding was that the 9CNA−Ar complexes were partially destroyed when oxygen gas was introduced together with Ar. Figure 2 compares the absorption and fluorescence excitation spectra in the presence and absence of oxygen at a total pressure of 300 Torr. When oxygen was added, the van der Waals complexes associated with 1−3 Ar atoms disappeared partly in both absorption and fluorescence spectra; cf. Figure 2, middle. A further increase of the partial pressure of oxygen at the same total pressure led to the total elimination of these bands (Figure 2, right). Accordingly, the intensity of the 0−0 band of the bare molecule was increased to the same extent in both the absorption and fluorescence excitation spectra. Since the van der Waals complex bands disappeared in the absorption spectra as well, the disappearance of the complex bands cannot be attributed to the quenching of the fluorescence of the complexes by oxygen, but rather indicates that the 9CNA−Ar complexes are not formed at all when oxygen is present in the cooling gas.

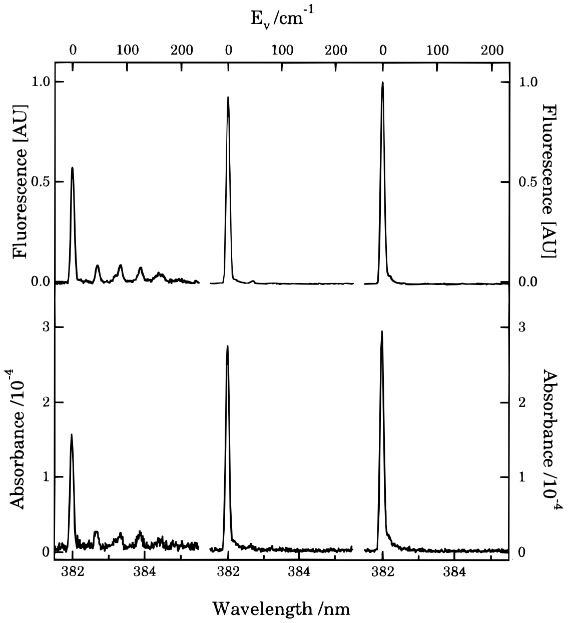

Figure 2. Absorption spectrum (bottom) and fluorescence excitation spectrum (top) of 9CNA seeded in Ar (left) and a mixture of Ar and oxygen (middle and right). The total pressure was kept at 300 Torr. The partial pressure of oxygen was 60 Torr (middle) and 220 Torr (right), respectively. The complexes with two and three Ar atoms coordinated disappeared partially in both absorption and fluorescence spectra. The intensity of the electronic origin band was increased nearly 2-fold for either spectrum upon adding oxygen.

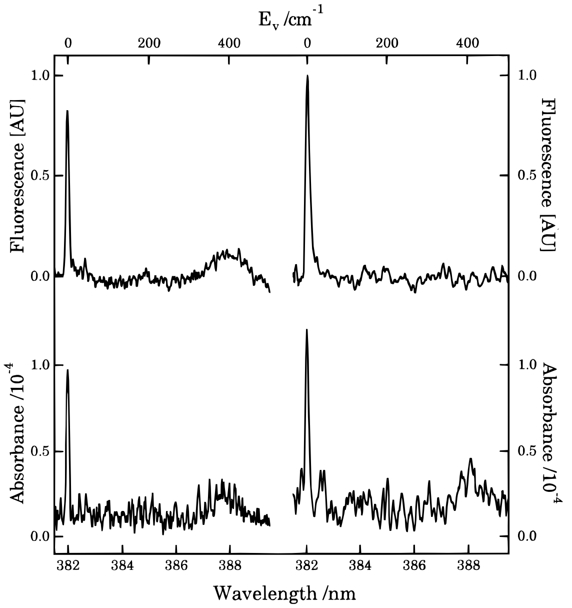

Figure 3. Absorption spectrum (bottom) and fluorescence excitation spectrum (top) of 9CNA seeded in Ar (left) and a mixture of Ar and oxygen (right). The total pressure was 900 Torr in both cases. The partial pressure of oxygen in the mixture was 250 Torr. The cone-shaped nozzle with a diameter of 200 μm was used. The broad spectral band at around 388 nm can be assigned to relatively large Ar clusters whose fluorescence quantum yield is approximately unity.

There remains the question how oxygen interacts with larger 9CNA−Ar clusters. When the backing pressure of Ar was increased to 900 Torr, a broad band was observed for both absorption and fluorescence excitation spectra, with its center shifted to the red by approximately 6 nm from the electronic origin band of the bare molecule; see Figure 3, left. This new band is due to rather large 9CNA−Ar clusters with coordination numbers not less than 20.[23] Unfortunately, the rotary pump and the volume of the vacuum chamber employed in the present experimental setup are small, and as a result, for a higher backing pressure the nozzle open time had to be chosen very short, which led to a low signal-to-noise ratio. Due to this and partly due to the increased cluster formation, the intensity of the 0−0 band was greatly reduced. The absorption and fluorescence excitation spectra showed a relative fluorescence quantum yield for this broad band, which is approximately unity. This is to be expected from the fact that the fluorescence lifetime measured for this broad band is close to the radiative lifetime.[23] When oxygen was added, the absorption spectrum still showed some absorption at this broad-band position (Figure 3, right) and a slight increase of the 0−0 band, but the signal-to-noise ratio was too low to specify quantitatively to what extent the broad band is reduced. On the other hand, this broad band disappeared below the noise level in the fluorescence excitation spectrum. It is suggested, therefore, that the fluorescence of the large 9CNA−Ar clusters was quenched by oxygen molecules. A large number of Ar atoms surrounding the 9CNA molecule appear to work as a sort of microscopic solvent that can dissolve molecular oxygen. The oxygen molecule thus bound to or accommodated within this cluster must be located close enough to 9CNA to quench the fluorescence upon photoexcitation. Still there is no direct experimental evidence for the formation of 9CNA−O_2 van der Waals complexes.

A large number of investigations have been carried out so far to explain the mechanism of the fluorescence quenching by molecular oxygen in solution, as well as in the gas phase. The values for the rate constant for the fluorescence quenching of the excited singlet state of many anthracene derivatives by oxygen in solution, k_q^s, are very large and limited only by the rate of the translational diffusion. This implies that the energy of an electronically excited molecule is instantaneously transferred to the molecular oxygen or that a nonemissive intermediate is formed. Furthermore, the oxygen could induce efficient intersystem crossing to an isoenergetic triplet state as is observed for many systems of anthracene derivatives and heavy atoms. The value of k_q^s for 9CNA in *n*-hexane solution is 9.0×10^9 M^{-1} s^{-1}.[27] From this large value it can be expected that the net intermolecular force between the 9CNA molecule and oxygen in solution is surely attractive. In the isolated molecule limit in the supersonic free jet, the high polarizability of oxygen ($\alpha = 1.6 \times 10^{-24}$ cm^3)[25] suggests a strong electric interaction with the aromatic molecule as well. This is further supported by the findings that the cooling efficiency was rather high when oxygen alone was used as a seeding gas or that the cooling was improved when oxygen was used in a mixture with other seeding gases.

There exists the possibility that the potential well for an oxygen complex is very shallow in the ground state, with the stabilization energy being less than 8 kJ mol^{-1} as given in the Introduction. As a result, only a very weak interaction between the target molecule and molecular oxygen would occur, and any complexes would hardly be formed or would immediately dissociate due to thermal energy remaining in the ligands. In the case of A−Ar van der Waals complexes, the binding energy is in the range of 600 cm^{-1},[28] corresponding to 7.2 kJ mol^{-1}. When we recall the finding, as shown in Figure 2, that no complexes with Ar were formed upon adding oxygen, it seems likely that the complexes of oxygen with 9CNA in the ground state are not formed at all. However, this potential well could be much deeper in the excited state and deep enough to produce an exciplex upon collision with oxygen. The transition could either be to a locally excited (LE) state that is coupled to a charge-transfer (CT) state or directly to the CT state if the transition is allowed. In the jet at the time of passing the interrogating light beam, the molecules are already in an isolated, collision-free condition, and complex formation under this condition hardly occurs. Such an exciplex formation[18,20,29] could account for the fact that no oxygen van der Waals complexes were found, and yet the quenching rate constant by oxygen is very high in solution.

On the contrary, the complex could in fact be well stabilized in the ground state, and stable complexes would be formed in the jet experiment. However, if the net force in the excited state is repulsive for every intermolecular distance of the heteromer, this would result in a very low oscillator strength for the absorption transition and, hence, would account for the missing of oxygen van der Waals complex bands in the absorption spectra. Nevertheless, such a stable complex formation in the ground state would lead to a measurable decrease of the intensity of the electronic origin band of the bare molecule when adding oxygen to the seeding gas. However, this behavior was not found at all in the experiments for various seeding gases and experimental conditions.

It has to be stated that the quenching mechanism in solution could theoretically be solely due to collisional energy transfer between the parent molecule and molecular oxygen, and the formation of an intermediate between the two would not necessarily be required. On the other hand, the temporal characteristics of the fluorescence quenching by oxygen of different anthracene derivatives in solution suggest that an intrinsic bimolecular reaction must be present (cf. ref 27 and references therein). A strictly diffusion-limited quenching reaction caused by collisional quenching could not account for the large variation of the quenching rate constant in solution.

B. Complexes of 9CNA with Iodine and Carbon Dioxide. So far we have not yet found a convincing reason for the lack of complex formation with oxygen. Two more small ligands were investigated to further elucidate this very intriguing behavior and to answer the question of how they collate to oxygen.

Iodine (I_2) was chosen as another diatomic ligand. It has a very high polarizability of $\alpha = 11 \times 10^{-24}$ cm^3 [30] and easily forms complexes with rare gases.[31] Furthermore, it is a good quencher in solution.[32] Figure 4 shows the absorption and excitation fluorescence spectra of 9CNA seeded in a mixture of Ne and I_2. The iodine vapor pressure at room temperature was calculated to be approximately 0.2 Torr. Three new spectral bands on the low-energy side can be distinguished. The band at 386.35 nm with a red shift of 4.3 nm ($\Delta\nu = 290$ cm^{-1}) could be safely attributed to 1:1 9CNA−I_2 van der Waals complexes of the vibrationless 0−0 transition. This assignment was confirmed in the inset, where the fluorescence excitation spectrum was taken without I_2. As Ne did not form any complexes within the applied pressure range, the very weak band, which is resolved only in the fluorescence excitation spectrum and is red-shifted by 3.4 nm ($\Delta\nu = 226$ cm^{-1}) from the origin, is assigned to a hot band of the bare 9CNA molecule.[19] The third band at 383.15 nm ($\Delta\nu = 74$ cm^{-1}) is the van der Waals complex band associated with the vibrational band of the bare molecule at 379.0 nm.

When Ar was used as a seeding gas, the progression of 9CNA−I_2−Ar_n complexes with $n = 1-3$ was observed on the low-energy side of the 9CNA−I_2 complex band, which can be clearly seen in Figure 5. The complex bands of the vibrationally excited molecule interfere partly with the 9CNA−Ar satellite bands. The bands associated with the I_2 complexes were greatly reduced when the vessel containing I_2 was cooled to 0 °C, at which the vapor pressure of I_2 is only 0.03 Torr. The fluorescence quantum yield for the electronic origin band of these complexes is approximately unity, since the ratios of the absorption and fluorescence excitation band heights at these bands are unity when normalized with the corresponding values

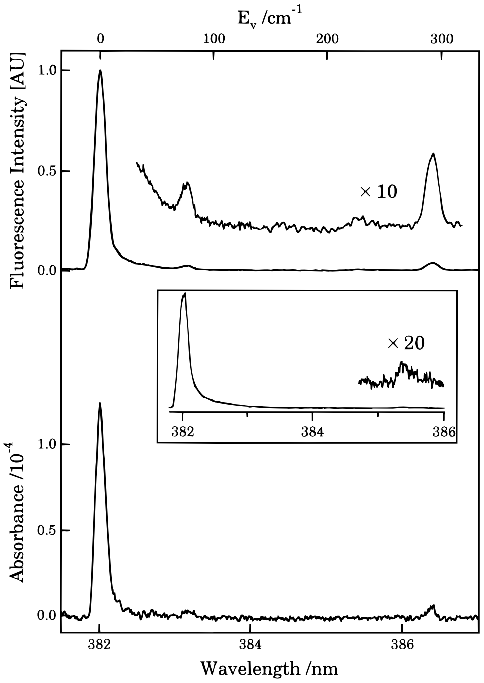

Figure 4. Absorption spectrum (bottom) and fluorescence excitation spectrum (top) of 9CNA seeded in a mixture of I_2 (0.2 Torr) plus Ne (490 Torr). The fluorescence excitation spectra are displayed in two intensity scales, as marked in the figure. The inset portrays the fluorescence excitation spectrum in the absence of I_2. The spectral feature in the inset, with a red shift of 226 cm^{-1} with respect to the 0−0 band, is a hot band of the parent molecule. The bands at 386.35 and 383.15 nm in the spectra with I_2 present can be safely ascribed to the 9CNA−I_2 1:1 complex of the vibrationless 0−0 transition and of the vibrationally excited bare molecule at 379.0 nm, respectively.

of the 0−0 band of the bare molecule. Even the complex band at 380.9 nm associated with the 12_0^1 band showed a large fluorescence quantum yield, although no accurate value can be derived from the data. Therefore, in order to account for the efficient nonradiative decay channel in solution, a vibronic-level-dependent fluorescence quenching has to be considered similar to the mechanism found for 9CNA in the supercritical fluid of Xe.[33]

What could be the reason for the finding that I_2 forms van der Waals complexes with 9CNA but oxygen does not? The spectra in Figures 4 and 5 indicate that the complex formation with I_2 is not very favorable as compared with Ar or Xe, and the associated band feature is small though detectable. Presumably, the large polarizability of I_2 leads to an energetically well-stabilized ground state. The energy interval between consecutive vibrational levels is only 214 cm^{-1} for I_2 because of its large mass. This is in sharp contrast to oxygen whose corresponding interval is 1580 cm^{-1}. When the temperature of the nozzle is 400 K, 99.7% of the oxygen molecules will be found in the zero-point vibrational state, whereas many I_2 molecules occupy the first few vibrational states. However, it is unknown how much of this internal rotational and vibrational energy is sapped away from these diatomic molecules by the rare gases upon expansion into the vacuum under the present experimental conditions. When the nozzle was heated to 450 K, the experiment showed that the intensity of the 9CNA−I_2 complex band indeed decreased below the noise level of the absorption and fluorescence signal.

As pointed out in section A, the potential well of the interaction between the parent molecule and oxygen is probably very shallow. Hence, it is interesting to assess how strong this interaction has to be in order to be detected in the experimental setup employed in this work.

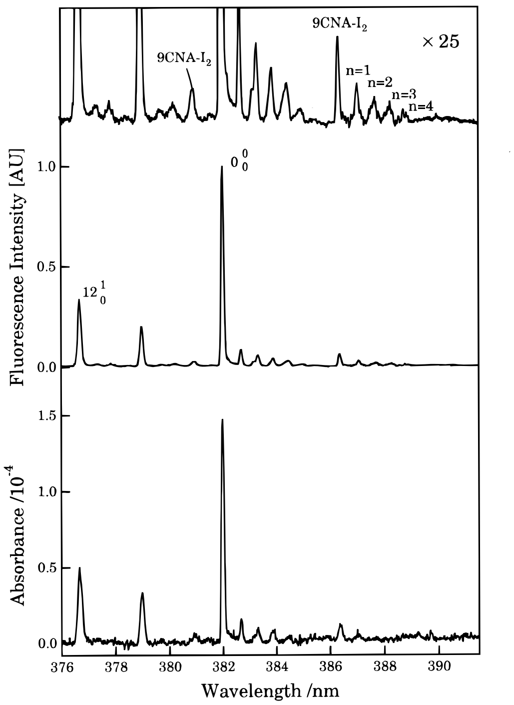

Figure 5. Absorption spectrum (bottom) and fluorescence excitation spectrum (top, two different intensity scales) of 9CNA seeded in a mixture of iodine (0.2 Torr) and Ar (300 Torr). The vibrational fundamental bands of the bare molecule are denoted 0_0^0 and 12_0^1. The plausible coordination numbers *n* for the 9CNA−I_2−Ar_n complexes are given in the figure. The quantum yield for all complex bands was approximately unity. The 9CNA−I_2 1:1 complex band associated with the 12_0^1 band can be distinguished in both spectra. However, the complex band associated with the vibrational band at 379.0 nm is buried in the 9CNA−Ar_n bands.

For the benzene−CO_2 complex and the naphthalene−CO_2 complex, the dissociation energies in the electronic ground state were recently theoretically calculated by Shen et al.[34] to be on the order of 12−16 kJ mol^{-1}. This value is reckoned to be approximately the same for the A−CO_2.[35] This must be large enough to form van der Waals complexes in a supersonic free jet. As a further test, van der Waals complex formation between 9CNA and CO_2 was investigated. CO_2 is a triatomic, nonpolar, linear molecule which has a high dynamical ionic polarizability of $\alpha = 2.63 \times 10^{-24}$ cm^3. Although the cooling efficiency upon supersonic expansion is rather low, a bathochromically shifted band that is ascribed to the 1:1 complex could be observed as is shown in Figure 6. The coordination of one CO_2 molecule caused an energy shift of approximately 140 cm^{-1} with respect to the 0−0 transition band. A comparison of the absorption and fluorescence excitation spectra in the magnified part of the spectra in Figure 6 showed that the fluorescence quantum yield of the complex is approximately unity. This is also to be expected from the fact that the fluorescence lifetime for the thermalized molecules in the supercritical fluid of CO_2 is comparable to the natural radiative lifetime.[33] Increasing the backing pressure to 900 Torr led to a sharp decrease in the intensity of the electronic origin band, which was ascribed to the formation of larger clusters.

Since the polarizability of 9CNA is only slightly higher than that for anthracene,[30b] the stabilization energy for the 9CNA−CO_2 in the ground state is likely to be of the same magnitude. We can therefore state that, for CO_2 complexes, a potential depth of 12−16 kJ mol^{-1} is deep enough to produce a detectable amount of van der Waals complexes under the present experimental conditions.

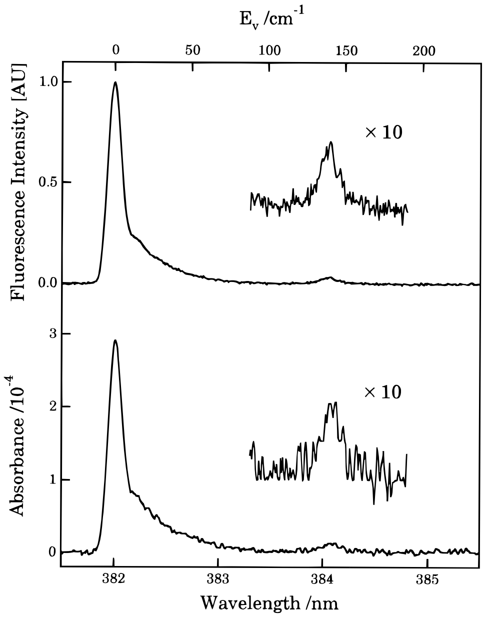

Figure 6. Absorption spectrum (bottom) and fluorescence excitation spectrum (top) of 9CNA seeded in CO_2 at a pressure of 500 Torr. The energy shift of the complex band is 140 cm^{-1}. The broad shoulder of the electronic origin band indicates a rather poor cooling efficiency. The magnified complex bands show that the fluorescence quantum yield of the 1:1 van der Waals complex is approximately unity.

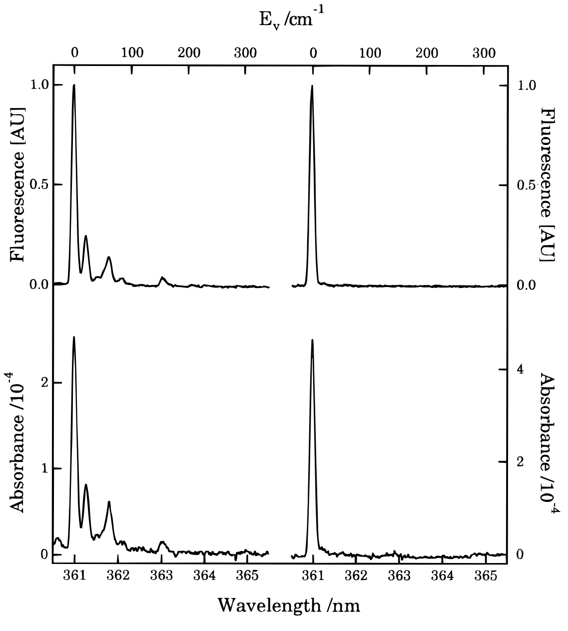

Figure 7. Absorption spectrum (bottom) and fluorescence excitation spectrum (top) of anthracene seeded in Ne (left) at a pressure of 500 Torr and a mixture of Ne and oxygen (right) with respective partial pressures of 450 and 50 Torr. The addition of oxygen removed the hot bands to a great extent, with no new band feature assignable to oxygen complexes.

C. Complexes of Anthracene with Oxygen. The values of k_q^S for oxygen in solution vary from anthracene derivative to derivative.[27] For instance, the value for anthracene is about 3 times larger than that for 9CNA, which may suggest a stronger interaction with the oxygen molecule. Hence, it could be speculated that oxygen van der Waals complexes could be found more readily for anthracene. The experiments were therefore repeated with anthracene and various mixtures of rare gases and oxygen.

However, the experimental results were approximately the same as with 9CNA; cf. Figure 7. When Ne alone was used as a seeding gas (Figure 7, left), several bands on the low-energy side of the electronic origin located at 361.1 nm were observed. These extra bands could be ascribed to vibrationally hot molecules.[36,37] Upon adding oxygen, the cooling efficiency was dramatically improved (Figure 7, right), and nearly congestion-free spectra were obtained. A similar result was obtained when oxygen was replaced by another diatomic molecule, N_2, although the cooling efficiency of N_2 alone was not as high as that of oxygen.

When Ar was employed as a seeding gas, the hot bands were still present, which made it difficult to assign the A−Ar complex bands. Again, the addition of oxygen removes these bands to a great extent. When oxygen alone was used as a seeding gas, the cooling was quite satisfactory. However, under all experimental conditions, no new spectral feature assignable to $A-O_2$ complexes could be found in the scanned wavelength range of 355 to 370 nm. Furthermore, the ratio of the absorption and fluorescence emission intensity at the electronic origin remained constant when the partial pressure of oxygen was varied. This indicates that a coincidental overlap of the electronic origin band of the bare molecule and its associated complex band can be ruled out.

Summary

The experimental results presented showed no spectral evidence for the van der Waals complex formation between oxygen and either of the host molecules, 9CNA or anthracene. Whereas these host molecules formed readily complexes with the rare gas atoms Ar and Xe, 9CNA also formed complexes with the diatomic molecule I_2 and the triatomic molecule CO_2. CO_2 was found to form complexes in spite of its inefficiency in cooling the host molecules. This is in accordance with the calculated large stabilization energy of the complex in the ground state.

The maximum backing pressure of the seeding gas applicable in our present system cannot exceed 1000 Torr. One has to bear in mind that, for instance, N_2 proved to be an efficient vibrational cooler[36] at a backing pressure of 2500 Torr. This pressure yielded remarkably congestion-free spectra whereas at lower pressures of up to 1000 Torr the cooling efficiency of N_2 was very low. Although O_2 cooled satisfactorily, even in the low-pressure range employed in this work, the expansion conditions at higher pressure might be more favorable for van der Waals complex formation.

We cannot explain the complete lack of any complex formation with oxygen yet. Nevertheless, some mechanism must prevent oxygen from forming complexes with A or 9CNA, even under supersonic jet expansion. The high cooling efficiency in the supersonic free jet, and the high quenching rate constants of the fluorescence in solution and in the gas phase, indicate an attractive interaction of the molecular oxygen with the host molecule in the ground state as well as in the excited state, though no complex formation could be found in the supersonic free jet. A very low stabilization energy in the ground state and an exciplex formation upon collisional (in the gas phase) or diffusional (in solution) encounter between an excited host molecule and molecular oxygen could account for the large quenching rate constant, though such an energy transfer does not necessarily require an intermediate to be formed prior to the energy transfer. For the supercooled molecules in the jet, this type of encounter is rare or even absent, which could explain the failure to observe complex bands in the spectra. Further research on theoretical calculation of the potential well of the complex in both ground and excited states might lead to a thorough insight into the mechanism of the interaction of molecular oxygen with aromatic molecules.

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