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Photodissociation of ND_3 and ND_2H at 193.3 nm: Symmetry dependence of the rotational distributions and vibrational excitation of the ND_2 ($\tilde{A}^2A_1$) fragment

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ABSTRACT

A rotational and vibrational analysis has been made of the ND_2 $\tilde{A}^2A_1 - \tilde{X}^2B_1$ emission spectrum produced from the ultraviolet laser induced dissociation of both jet cooled and room temperature deuterated ammonia, ND_3, and di-deuterated ammonia, ND_2H. The pattern of the strong features in the emission spectra is very different in the fragmentation of ND_3 and ND_2H, with a much wider range of angular momentum states being observed from the photolysis of the predissociative ($\tilde{A}$) state of unsymmetrical parent ND_2H ($\tilde{A}$). The analysis is based upon the earlier studies of the electronic spectrum of ND_2, and model calculation based upon the stretch-bender Renner–Teller Hamiltonian. The spectra consist of two types, transitions from a narrow distribution of high angular momentum states in the photolysis of ND_3 and ND_2H, and in the photolysis of ND_2H strong emission from threshold states in three high energy regions. The threshold states are in the third bending level, $v_2' = 3$ of the ND_2 ($\tilde{A}$) state, and have no angular momentum about the axis of least moment of inertia, $K_a' = 0$.

1. Introduction

The electronic spectrum of the NH_2 free radical was one of the first examples of the use of high resolution spectroscopy to study a transient polyatomic molecule. This absorption spectrum was recorded, following the flash photolysis of ammonia, NH_3, by Ramsay [1]. Following a further note by Dressler and Ramsay [2] on the role that NH_2 played as an example of the Renner effect [3], they published a detailed analysis of the electronic absorption spectra of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition in NH_2 and ND_2 [4]. In this paper they made a comparison of the experimental energy level pattern with that calculated by Pople and Longuet-Higgins [5], which showed clearly the role played by Renner, or now more commonly Renner–Teller, coupling.

Since this seminal paper [4] in 1959, with the exception of one paper by Muenchausen et al. in 1985 [6] on electronic and vibrational spectra of ND_2, and a detailed study by Morino and Kawaguchi [7] of the high resolution far infrared spectra of NH_2, NHD and ND_2, little work was done on the spectroscopy of ND_2, particularly electronic spectroscopy, although the electronic spectrum of NH_2 has been studied extensively [8–12]. The Experiments carried out on ND_2 in the period since 1988 have been primarily concerned with studying the photodissociation dynamics of ammonia and its isotopologues. The first measurements [13,14] were carried out by Mordaunt et al. by H(D) Rydberg atom photofragment translational spectroscopy. A detailed theoretical model of the photodissociation dynamics was given by Dixon [15]. These studies were followed by a series of papers [16–20] on the vibrational dynamics of the photofragmentation of NH_3, NH_2D, ND_2H and ND_3, by Leone and his colleagues, who studied the photofragmentation in detail using Fourier transform spectroscopy of the emission from the triatomic fragment molecules.

More recently a detailed analysis has been made of the fluorescence spectra of ND_2 obtained by the photolysis of ND_3 [21] using an excimer laser operating at 193.3 nm. In the present paper this analysis has been extended to the emission spectra of ND_2 obtained by the photolysis of ND_2H. In the comparison of the emission spectra of ND_2 produced by the photolysis of ND_3 and ND_2H Mordaunt et al. [13,14] and Reid et al. [17,18,20] have shown that the differing fragmentation energies of the NH bond in ND_2H and the ND bond of ND_3 need to be taken into account. The available energy from the excimer laser corresponds to ca. 51 733 cm^{-1}. The bond dissociation energy of the NH bond of ND_2H given by Mordaunt et al. [12,13] corresponds to 37 300 cm^{-1}, whereas that of the ND bond in ND_3 is equivalent to 38 010 cm^{-1}. Since the lowest ro-vibronic level in the A state of ND_2 lies at 11 120 cm^{-1} the excess energy for populating excited rovibronic levels of the A state of ND_2 is 3313 cm^{-1} from the fragmentation of ND_2H, but only 2603 cm^{-1} from ND_3 fragmentation. As a result the highest wavenumber spin doublet observed from the emission of ND_2 from the jet cooled ND_3 parent is a very weak doublet at 13 391 cm^{-1} due to $2_0^1\ {}^{P}P_{7,7}$.

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One of the complications of the analysis of the emission spectrum of ND_2 is that none of the energy levels in the $\tilde{A}^2A_1$ state of ND_2, from which emission has been recorded, correspond to those observed by Dressler and Ramsay [4] in their absorption spectra. As a result of this no direct comparisons of the absorption and emission spectra may be made. Furthermore, many of the observed fluorescence spectra arise from states with high angular momentum about the molecular *a*-rotational axis, whereas the spectra recorded by Dressler and Ramsay [4] accessed only vibronic levels up to $K' = 3$.

It is the purpose of the present paper to explore the effects that the photolysis of the unsymmetrical ND_2H exerts on the form of the observed emission spectrum, in particular to the reduction of the regularity of the pattern of the emission spectra of ND_2 from that observed from the photolysis of the symmetrical isotopologue ND_3.

The emission spectra recorded following the photolysis of ND_3 showed considerable repeating regularity in their structure [21], whereas those recorded following the photolysis of the unsymmetrical isotopologue, ND_2H, exhibit far less regularity in their repetitive structure. One possible hypothesis is that as the trigonal symmetry of the parent molecule has been broken, efficient transfer of energy to motion about the *b*/*c* rotational axes of the ND_2 is much more likely, and may account for some of the complexity of the emission spectrum.

2. Experimental

A detailed description of the experimental apparatus has been given in previous publications on the dissociation dynamics of ammonia and deuterated ammonias [16–20], so only a very brief summary will be provided here. The studies were performed both at room temperature, with a continuous flow of ND_3, or a mixture containing NH_3, NH_2D, ND_2H and ND_3, and jet cooled, with a piezo-electric pulsed valve. The triggering of the ArF eximer laser, which initiates the photodissociation, and also the opening of the pulsed jet for the jet cooled studies, were both synchronised to the position of a moving mirror in a commercial continuous scan

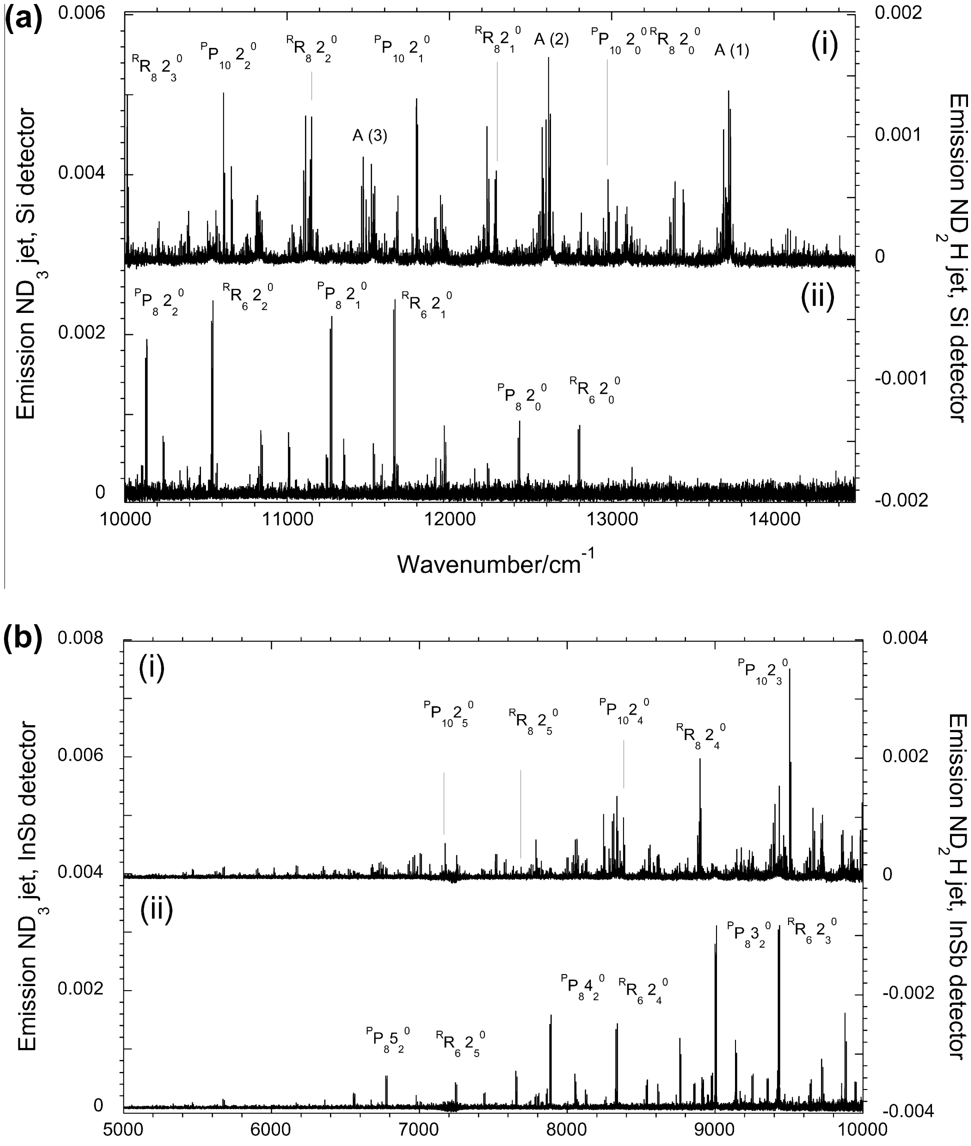

Fig. 1. Survey of the entire product emission spectrum of $ND_2(\tilde{A}^2A_1)$ from the photodissociation of: (i) jet cooled ND_2H and (ii) ND_3. (a) 10 000 to 14 450 cm^{-1}, Si avalanche detector; (b) 5000–10 000 cm^{-1}, InSb detector. Note the much greater density of the spectral lines in the spectrum of jet cooled ND_2H, and their high intensity at the onset of fluorescence. Features A(1)–A(3) comprise several transitions, including those from the $K'_a \equiv K' = 0$ levels of $v'_2 = 3$ in the $ND_2(\tilde{A}^2A_1)$ state.