Highly excited vibrational states of HCN around 30 000 cm⁻¹

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This article describes the analysis and interpretation of rovibrational spectra involving highly excited vibrational states in the molecule of HCN. The spectra were obtained by means of the vibrationally mediated photodissociation technique. Analysis of the spectra revealed four bands with Σ - Σ structures that, once fitted, provided the energies and rotational constants of four new, highly excited vibrational states in the region of the potential energy surface near and above 30 000 cm⁻¹. All the states could be identified with the help of a state-of-the-art variational calculation. Together with the states already observed in previous works, eight highly excited states have so far been identified in this region. © 2006 American Institute of Physics. [DOI: 10.1063/1.2387171]

I. INTRODUCTION

The molecule of HCN presents considerable interest in the fields of molecular spectroscopy and dynamics. From the theoretical point of view, HCN is a small linear molecule that constitutes an excellent test system for new models. Experimentally, its very high anharmonicity, typical of light hydrides, presents the advantage of allowing easy access to vibrationally excited states through the probing of overtone transitions, which has translated into the availability of large amounts of experimental data that map broad regions of the potential energy surface in the ground electronic state.¹⁻³ From the dynamics point of view, the HCN ↔ HNC isomerization reaction has also attracted the attention of numerous researchers in the field of unimolecular reaction dynamics. Given the existence of an energy barrier that separates the two minima of the potential energy surfaces of HCN and HNC,⁴ the study of excited vibrational states in HCN, especially those sporting a large number of bending quanta whose excitation could trigger the isomerization,⁵ is of special interest.

The present work deals with the analysis of rovibrational spectra obtained using a vibrational excitation technique that allowed us to register transitions involving excited states with energies as high as 30 000 cm⁻¹. The technique has been described in a previous work,⁶ in which some of the spectra obtained in the initial measurements were analyzed and the positions of a number of excited vibrational states were determined. In this article we report the result of the analysis of the remaining bands, which provide information about some previously unknown excited vibrational states in the vicinity of 30 000 cm⁻¹.

II. EXPERIMENT

The spectra analyzed for this work were obtained during the course of the measurements described in Ref. 6. Since all the relevant experimental details are treated in depth in the aforementioned article, we will only give here a brief experimental description in order to provide a general idea of how the spectra are obtained.

The experiment is based on the use of a vibrationally mediated photodissociation (VMP) scheme of the type pioneered by Ticich *et al.*,⁷ which in our case requires the sequential use of four photons of different wavelengths. Figure 1 presents a simplified representation of this four-step process. The first photon ("pump") is used to populate the (0,0,4) vibrationally excited state from the ground state. Note that, as in our previous work, we are using the "old" Herzberg labeling of the HCN vibrational normal modes, where ν_1 is predominantly a CN stretch, ν_2 is the bend, and ν_3 is predominantly a CH stretch.⁸ The second photon ("jump"), which arrives with a delay (typically 30 ns), further excites a fraction of the already excited molecules to a highly excited vibrational state with an energy close to 30 000 cm⁻¹, which corresponds to about 10–12 quanta of stretching vibration. Since these highly excited states are initially unknown, the wavelength of the laser that provides the jump photon is scanned in order to look for transitions between the well known (0,0,4) state and vibrational states present in the unmapped region around 30 000 cm⁻¹. The sample pressure (between 1 and 2.5 torr) was sufficiently high that there was considerable rotational relaxation and limited vibrational relaxation between the pump and jump pulses, allowing detection of a much richer spectrum than would be observed without relaxation. Only when the jump laser is in resonance with a transition starting from a level with term value near 12 600 cm⁻¹ are molecules with term values near 30 000 cm⁻¹ produced. After a brief delay (4 ns),

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FIG. 1. (Color online) Schematic of the VMP technique.

the third photon (“photodissociation”) selectively dissociates the highly excited HCN molecules to produce H and CN(A²Π) radicals. Finally, a fourth photon (“probe”) is used to detect the presence of the CN(A²Π) photofragments by electronic excitation to the CN(B²Σ⁺) state and subsequent detection of the strong fluorescent emission that takes place between the B²Σ⁺ excited state and the X²Σ⁺ ground electronic state of the radical. With this scheme, a fluorescence signal can be seen when a rovibrational transition is found between (0,0,4) and a highly excited state.

Four pulsed laser systems provide the four different photons required. Of these, only the jump laser wavelength is scanned, while the wavelengths of the other three remain fixed during the experiment. The pump laser wavelength is initially tuned to a well known rovibrational transition between the ground state and the (0,0,4) excited state in order to pump population to (0,0,4) with every pulse, and remains there for the rest of the experiment. The photodissociation beam is generated with a fixed wavelength of 355 nm [a harmonic of the Nd:YAG (yttrium aluminum garnet) laser that pumps the dye laser that generates the jump pulse], so that a photon carries enough energy to dissociate the HCN molecule from the highly excited vibrational state and reach the A²Π state of the CN photofragment, but not enough to reach the B²Σ⁺ state or to produce direct photodissociation from the ground vibrational state through a two-photon absorption. Finally, the probe beam wavelength is tuned to the most intense region—measured in Boltzmann equilibrium—of the CN(*v*=1,*B*)←CN(*v*=0,*A*) absorption band, which is also well known,⁹ and remains there for the

duration of the measurement. A delay of 400 ns is introduced between the photodissociation and probe pulses in order to allow the rotational population in CN(*v*=0,*A*) to approach the Boltzmann equilibrium, which maximizes the amount of population excited to the CN(*v*=1,*B*) state.

III. RESULTS AND ANALYSIS

Figures 2 and 3 present the two regions of the spectrum analyzed in this work, which we have named “region 1” and “region 2.” Each one of the experimental spectra in the figures is presented together with stick spectra that have been built using the experimental frequencies and intensities of the rovibrational lines, and that are shown here just for the sake of clarification by separately picturing the different bands analyzed in the two regions. The labels in the stick spectra already identify the states responsible for the transitions that give rise to each one of the bands.

Region 1 contains three different bands, one of which (labeled “band 3” in Fig. 2) corresponds to the tail of the *P* branch of an already known band.⁶ The other two (“band 1” and “band 2”), which present a clear *PR* structure and thus correspond to Σ–Σ transitions, are observed here for the first time and have been independently fitted following a standard procedure (five-parameter, *m*-polynomial free fit) to obtain the band origins and the rotational constants of the states implicated in the transition. Region 2 also contains two new Σ–Σ bands (“band 4” and “band 5”) that have been analyzed in the same fashion. At least a third band is also visible in region 2, showing a characteristic doublet pattern that suggests a transition of the Π–Π type. Unfortunately, most of the

FIG. 2. Region 1 of the spectrum.

FIG. 3. Region 2 of the spectrum.

few visible lines of this band are overlapping with a stronger band, a fact that prevented a successful analysis.

Once the bands were fitted, identification of the lower states was straightforward from the values of their rotational constants. These states are listed in Table I. The fact that the departure state of band 2 is not (0,0,4) is due to population of the departure (3,0,2) state through collisional relaxation from (0,0,4), an effect previously observed in these experimental conditions. The free fit used for the initial identification of the lower states was then repeated constraining their rotational constants and energies to their bibliographic values¹⁰ in order to obtain more accurate final parameters for the upper states.

Once their energies and rotational constants were available, identification of the upper states was carried out with the assistance of the variational calculation already described in our previous work,⁶ based on the use of the Carter-Handy-Mills potential energy surface.¹¹ The accuracy of the calculation made the identification straightforward for the upper states of three bands (bands 1, 3, and 4), since it provided very clear candidate states that could be unequivocally assigned. For the upper state of the remaining band (band 2), the calculation provided two very close candidate states in the region [(0,2,10) and (6,0,6)], but a rotational analysis showed that the small value of the experimentally determined rotational constant was consistent with a state without excitation in the bending vibration, and the state was identified as (6,0,6). In all cases, the variational calculations predicted that the eigenstates had wave functions with large

TABLE I. Observed bands and band origins.

Band structure	Transition	Origin (cm ⁻¹)
Band 1: $PR(\Sigma-\Sigma)$	(4,2,7) ← (0,0,4)	17 193.18(6)
Band 2: $PR(\Sigma-\Sigma)$	(6,0,6) ← (3,0,2)	17 221.75(6)
Band 4: $PR(\Sigma-\Sigma)$	(3,2,8) ← (0,0,4)	17 812.13(7)
Band 5: $PR(\Sigma-\Sigma)$	(5,0,7) ← (0,0,4)	17 918.24(7)

TABLE II. Energies (calculated and experimental) and rotational constants (experimental) of the observed excited states.

State	G_v^{calc} (cm ⁻¹)	G_v (cm ⁻¹)	B_v (cm ⁻¹)	D_v (cm ⁻¹)
(4,2,7)	29 830.23	29 829.07	1.3795(2)	...
(6,0,6)	29 872.82	29 879.62	1.3603(1)	$(5 \pm 2) \times 10^{-6}$
(3,2,8)	30 450.32	30 448.01	1.3779(3)	$(9 \pm 3) \times 10^{-6}$
(5,0,7)	30 543.19	30 554.13	1.3613(1)	$(2.3 \pm 0.3) \times 10^{-6}$

overlap (>86%) with a single contracted basis function that provided the normal mode assignment. Thus, these quantum number assignments are meaningful despite the very high level of excitation of the states involved.

Table I presents the assignments of the observed bands and their origins. Table II presents the calculated and experimental energies and the rotational constants (including the centrifugal distortion constant D when the data permit its determination) of the identified states. The agreement between calculation and experiment is excellent, especially when one considers the high energy region in which these highly excited vibrational states lie.

Figure 4 presents an arrow diagram summarizing all the

FIG. 4. (Color online) Arrow diagram showing the transitions and excited states observed with the VMP technique. The dark arrows represent transitions observed in this work, and the light arrows transitions observed in the previous work mentioned in the text. Term values (in cm⁻¹) are shown in italics.

transitions observed in both the present work and the previous one in which the VMP technique was already used on HCN,⁶ and all the states identified as participants in these transitions.

IV. CONCLUSIONS

The analysis of rovibrational spectra of HCN obtained with a four-photon VMP technique has allowed the identification of four new Σ - Σ bands and of the states responsible for these transitions. Three of the bands correspond to transitions departing from the initially populated (0,0,4) state, while the fourth one departs from (3,0,2), a nearby state that can only be populated by collisional relaxation from (0,0,4). The upper states of the four transitions, all of them observed for the first time, are located in the vicinity of 30 000 cm⁻¹ and have been identified with the assistance of a state-of-the-art variational calculation based on the Carter-Handy-Mills potential energy surface.

These results, together with the ones presented in Ref. 6, render a total of eight highly excited vibrational states that have now been observed and identified in the region between 29 270 and 30 540 cm⁻¹, an energy that corresponds to approximately 2/3 of the dissociation energy of HCN and almost a factor of 2 higher than the calculated barrier to isomerization.

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