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Gas-phase infrared spectroscopy on the lowest triplet state of the pyrazine–argon complex

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Abstract

The infrared (IR) absorption spectrum of the jet-cooled pyrazine–argon Van der Waals complex in its lowest triplet state is measured. Vibrational excitation of the laser-prepared triplet state by IR absorption causes dissociation of the complex, which is monitored via the depletion of the pyrazine–argon ion signal. A total of 10 vibrational transitions are detected in the 500–1500 cm^{-1} region. Comparison of these data with ab initio calculations might help to elucidate the nature of the distortion of the lowest triplet state by other electronically excited states. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Pyrazine is the most symmetric of the three diazabenzene. It has been studied extensively, using various spectroscopic techniques [1]. Of special interest is the lowest triplet state of pyrazine, which is found to play an important role in the photophysics of this molecule [2–10]. The vibrationless level of the T_1 state is found to lie 4056 cm^{-1} below that of the S_1 state. This leads to so-called 'intermediate-type' behavior that manifests itself in the observation of bi-exponential decay of excited levels in the S_1 state in time-domain experiments and in the observation of molecular eigenstates in frequency-domain experiments [7].

The T_1 state therefore has been the subject of many studies and has been identified as a ${}^3B_{3u}$ state of $n\pi^*$ character [11]. It has, however, not yet indisputably been established whether the potential surface of this state is distorted and what its symmetry is. Just as for the S_1 state [1], it has been suggested that the lowest triplet state of pyrazine is distorted due to vibronic coupling with one or more higher-lying B_{1u} or B_{2u} states of $\pi\pi^*$ character [12–15]. On the basis of studies on the $T \rightarrow S$ emission and $T \leftarrow S$ excitation of pyrazine in different crystals, Nishi et al. concluded that the potential surface of the triplet state should be described by a double minimum potential along the ν_5 and ν_{10a} normal coordinates in the crystal [12]. Several other groups also use vibronic coupling between the ${}^3B_{3u}(n\pi^*)$ state and higher lying $\pi\pi^*$ states via the ν_5 or ν_{10a} mode to explain their observations [13,14]. Kokai and Azumi suggested a distortion

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along the ν_4 coordinate to explain the observed phosphorescence spectra of pyrazine in a benzene crystal [15]. Nevertheless, more recent experiments failed to show any evidence for vibronic coupling to a $^3\pi\pi^*$ state or for a second low-lying triplet state [16,17]. This seems to be validated by ab initio calculations that predict the $^3B_{1u}$ state to be $\sim 1000\text{ cm}^{-1}$ higher in energy than the S_1 state [18].

Detailed information on the vibrational structure of the lowest triplet state is essential in order to validate any calculation on the triplet state, but, despite extensive studies, most assignments are restricted to the totally symmetric modes, although some overtones and combination bands of non-totally symmetric modes have been observed [13,16,19]. Recently, Kok et al. [20] measured the infrared (IR) spectrum of the $^3B_{3u}(n\pi^*)$ state of pyrazine in a dodecane matrix, using a free-electron laser. However, the nature of these experiments makes it difficult to determine which of the observed bands can be assigned to IR transitions in the triplet state. Furthermore, only gas-phase experiments can insure that the observed distortions are not matrix-induced.

The free-electron laser as a widely tunable IR source, in combination with mass-selective double-resonance ionization spectroscopy, has proven to be a powerful tool to do gas-phase IR spectroscopy on jet-cooled polyatomic molecules [21–23]. Experimentally it is often found to be easier to do measurements on complexes of these molecules with an inert gas. IR laser-induced vibrational predissociation of such weakly bonded complexes can be used to measure their IR spectra [22–27]. We have used this technique up to now to measure the IR spectra of the ground state of neutral and ionized Van der Waals complexes [22,23], but it can, as will be demonstrated, also be applied to measure pure IR gas-phase spectra of long-lived electronically excited states. The 'matrix-shift', induced by the additional argon atom, of vibrational transitions of the argon clusters compared to transitions in the bare molecule will, in general, be limited to a fraction of a percent of the corresponding frequency [28–30], and the spectra can well be simulated using ab initio calculations on the bare molecule [22,23]. Thus, instead of measuring the vibrational spectrum of the lowest triplet state of pyrazine, the spectrum of the triplet state of the pyrazine–argon complex is measured. The pure

IR frequencies and intensities that follow from these measurements can be compared to calculations on the $^3B_{3u}(n\pi^*)$ state of pyrazine to yield more information on the symmetry of this state and the possible coupling mechanisms that are involved.

2. Experimental

The molecular beam machine used for the experiments is described elsewhere [31]. It is currently installed at the 'free-electron laser for IR experiments' (FELIX) user facility in Nieuwegein, The Netherlands [32,33], and consists of a molecular beam apparatus, two tunable pulsed dye laser systems and a differentially pumped Wiley–McLaren-type linear time-of-flight (TOF) mass spectrometer. Pyrazine is put in the sample compartment of a pulsed valve (R.M. Jordan Co.), heated to 40°C and seeded in argon (2 bar backing pressure). Gas pulses are formed by expansion through a 0.5 mm diameter orifice into vacuum of 10^{-6} Torr. The molecular beam is skimmed about 4 cm downstream upon entering the interaction region. In this region, the molecules can be excited and subsequently ionized by two separately pumped dye lasers. To do the IR experiments, the output of FELIX enters the interaction region counterpropagating the two dye laser beams via a vacuum tube that is connected to the molecular beam spectrometer. It is aligned, both in space and time, in between the two dye lasers. The laser beam axis, the molecular beam axis and the TOF tube axis are mutually perpendicular. Ions generated in the interaction region are extracted and accelerated to a microchannel plate detector, the signal of which is amplified and fed into a digital oscilloscope (LeCroy 9430), connected to a PC. A four-channel digital delay/pulse generator (SRS DG535) is used to synchronize the molecular beam spectrometer to the FELIX output to nanosecond precision. The whole system runs at a 10 Hz repetition rate.

FELIX consists of two lasers: the first, FEL-1, generating IR radiation with an energy between 40 and 400 cm^{-1} and the second, FEL-2, generating radiation between 300 and 2000 cm^{-1} . This radiation appears in the form of macropulses of about 4 μs duration, containing up to 100 mJ of energy.

Each of these pulses is made up of a train of micropulses that are 0.3–5 ps long and 1 ns apart. For the experiments reported here only FEL-2 is used, at a macropulse repetition rate of 10 Hz and a bandwidth of typically 0.5–1.0% of the central frequency. To induce the $T_1 \leftarrow S_0$ transition in the pyrazine–argon complex, laser radiation at 373 nm, generated by frequency doubling the output of a Nd:YAG pumped pulsed dye laser system in a KDP crystal, is used. For subsequent ionization of the laser-prepared triplet state of the complex, laser radiation at 208 nm, generated by frequency mixing the fundamental and the doubled frequency of a similar dye laser system, is used.

First, an attempt was made to measure the IR absorption spectrum of the lowest triplet state of bare pyrazine. For this the first dye laser excites the vibrationless triplet state at 26820 cm^{-1} [1], while the ionization laser is tuned to further excite the molecule to just below the ionization potential (74908 cm^{-1} , determined via the S_1 origin) [34]. Since in the first step a long-lived triplet state is excited, the time-delay between the two dye lasers can be as long as $5 \mu\text{s}$. Ionization can only be achieved if an additional resonant IR photon excites a vibration in the triplet state that subsequently can be ionized by the ionization laser. This scheme, however, did not yield any detectable ion signal, probably due to unfavorable Franck–Condon overlap between excited vibrations in the triplet and ionic ground states.

We then decided to do measurements on the pyrazine–argon complex instead, by using the excitation scheme given in Fig. 1. Again, the first dye laser excites the vibrationless triplet state (shifted by about 16 cm^{-1} from the $T_1 \leftarrow S_0$ transition of pyrazine) [13], but now the ionization laser ionizes the cluster to yield a pyrazine–argon ion signal. By scanning the first dye laser over the triplet transition and fixing the ionization laser just above the IP, the rotational contours of the triplet transition of pyrazine and its complex with argon are measured. From a simulation of the rotational contour spectra, which yields the relative origins, the origin of the $T_1 \leftarrow S_0$ transition is found to be 16.6 cm^{-1} red-shifted from the same transition in pyrazine. For the actual experiments, the excitation laser is set on the central part of the rotational contour of the complex. Whenever the

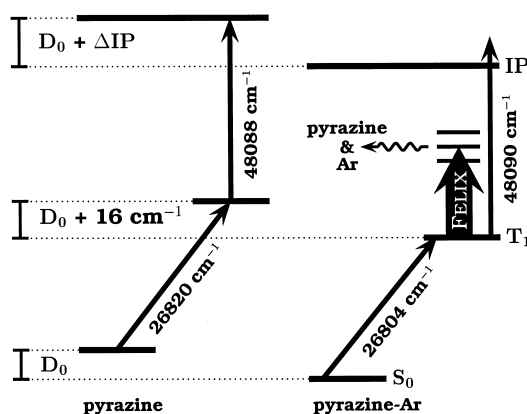


Fig. 1. Energy level scheme of pyrazine and pyrazine–argon, indicating the experimental detection method. IR laser-induced pre-dissociation of the pyrazine–argon clusters in their triplet state is monitored via depletion of the ion signal on the parent mass of the complex.

IR laser, that is fired in between the two dye lasers, excites a vibrational level above the dissociation limit in the triplet state, the pyrazine–argon cluster can dissociate and the ion signal will decrease. Thus, the IR absorption spectrum of the triplet state is measured as a depletion of the pyrazine–argon ion signal.

3. Results

The measured IR spectrum of the lowest triplet state of the pyrazine–argon complex, recorded via the scheme given in Fig. 1, is given in the upper panel of Fig. 2. The spectrum shown in Fig. 2 is the result of several different scans. Since the IR spectrum is measured as a depletion of the pyrazine–argon signal, the signal S of each of the scans is given by:

$$S(\nu) = a e^{-\sigma(\nu)I(\nu)}, \quad (1)$$

where I is the IR laser power, σ the absorption cross-section and a is the pyrazine–argon signal generated by the UV lasers when no IR light is present. Each scan is corrected for fluctuations in IR laser power to yield a pure absorption spectrum. One scan was taken with a laser power attenuation of 30 dB to avoid saturation of the strong absorption line around 700 cm^{-1} .

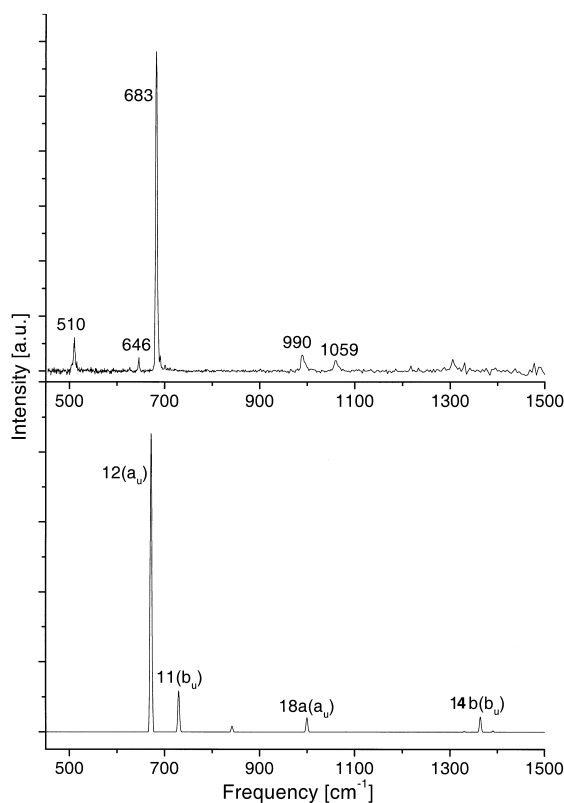


Fig. 2. Observed absorption spectrum of pyrazine–argon as a function of IR laser frequency (upper panel), compared to the calculated IR spectrum of pyrazine in its triplet state (lower panel).

For comparison a calculated absorption spectrum of bare pyrazine is shown in the lower panel of Fig. 2. This calculation is performed with GAUSSIAN 94 [35], using a Becke3LYP functional with the D95(d,p) basis set. Calculations assuming D_{2h} symmetry did not yield a minimum on the potential energy surface at this level of theory, so C_{2h} symmetry was assumed for the $^3B_{3u}$ state. The calculated frequencies are given in Table 1, together with assignments of previously measured vibrations and their irreducible representations in the C_{2h} point group. The frequencies and relative intensities of the measured IR transitions are also given in this table. Since the measurements concern the pyrazine–argon complex, we might expect to see Van der Waals modes showing up as sidebands of the strong transitions. The rather weak modes at 691 or 701 cm^{-1}

might be attributed to this. Besides this, still more vibrational transitions show up in the spectrum than are predicted by the calculations, where, using C_{2h} symmetry, a total of 8 a_u and b_u vibrations are IR active in this frequency range but only five of them are calculated to have reasonable intensity. Possibly

Table 1

Experimental and calculated vibrational frequencies (cm^{-1}) in the lowest triplet state of pyrazine. Calculations were performed using GAUSSIAN 94 (Becke3LYP/D95(d,p)). The intensity of the strongest observed IR transition is taken to be the same as the strongest calculated transition, which is given in $km\ mol^{-1}$

Frequency		IR intensity		Assignment
Exp. (cm^{-1})	Calc. (cm^{-1})	Exp. ($km\ mol^{-1}$)	Calc. ($km\ mol^{-1}$)	
237 ^a	272		34	16b(b_u)
406 ^b	440		0.2	16a(a_u)
440 ^a	208			10a(a_g)
510 ^c		89		
522 ^a	809			5(b_g)
557 ^a	374			4(b_g)
563 ^b	730		117	11(b_u)
620 ^a	614			6a(a_g)
	621			6b(b_g)
646 ^c		36		
683 ^c	672	853	853	12(a_u)
691 ^c		41		VdW?
701 ^c		16		VdW?
	842		17	17a(a_u)
	1000		41	18a(a_u)
980 ^a	1019			1(a_g)
990 ^c		43		
	1016			3(b_g)
1059 ^c		28		
	1082		1	18b(b_u)
1146 ^a	1199			9a(a_g)
	1306			8b(b_g)
	1330		2	19b(b_u)
	1364		43	14(b_u)
	1391		2	19a(a_u)
1230 ^a	1558			8a(a_g)
1305 ^c		31		
1330 ^c		22		
1478 ^c		21		
	3197			7b(b_g)
	3199		12	13(a_u)
	3228		1	20b(b_u)
	3229			2(a_g)

^a Ref. [16].

^b Ref. [19].

^c This work.

vibronic coupling of the ${}^3B_{3u}(n\pi^*)$ state to higher-lying ${}^3\pi\pi^*$ states will have to be taken into account in the calculations in order to fully reproduce all the observed transitions. Possible Fermi resonances could further complicate the spectrum. Based on the calculations reported here, which at least reproduce the strong transition observed at 683 cm^{-1} , we assign this transition to the ν_{12} mode of a_u symmetry.

4. Conclusion

IR absorption spectra of jet-cooled Van der Waals complexes in their triplet state can be measured using a 'standard' molecular beam apparatus in combination with a free-electron laser, as demonstrated here by recording the pure IR absorption spectrum of the pyrazine–argon complex in its lowest triplet state. A total of 10 IR transition is observed in the range from 500 to 1500 cm^{-1} . The strongest of these transitions is assigned to the ν_{12} mode of a_u symmetry, but, so far, no other assignments can be made. Due to a distortion of the potential energy surface of the triplet state of pyrazine, caused by vibronic coupling to other electronic states, the Becke3-LYP/D95(d,p) calculations performed using C_{2h} symmetry for the triplet state are unable to reproduce all the observed features in the IR absorption spectrum. The reported spectra, however, are expected to make an essential contribution to the validation of ab initio calculations on the triplet state of pyrazine.

In future experiments, the information obtained from the IR spectrum of the lowest triplet state of pyrazine will be used to access the vibrational levels of the lowest triplet state of pyrazine via its eigenstates in the lowest singlet state in a UV–IR double-resonance experiment.

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