Gas Phase Two-Photon Spectroscopy of Polyazines: Pyrazine

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The two-photon excitation spectra of gas phase pyrazine-h_4 and -d_4 in the region of the $S_1 \leftarrow S_0$ transition are presented. The two-photon absorption which is electronically forbidden is induced by various vibrations of ungerade parity. Because of the different selection rules for two-photon transitions hitherto unknown vibrational frequencies in the excited state $^1B_{3u}$ have been determined.

It has been extensively demonstrated for the case of benzene that high resolution two-photon absorption spectroscopy can yield novel spectral information about electronically excited states due to its selection rules [1]. In the case of benzene the calculation of a good force field for the first electronically excited state was even possible [2] on the basis of this new information. Such new information is also expected for the case of pyrazine.

Previous two-photon work on pyrazine in the solid phase presented only shifted vibrational frequencies [3] because of the interaction in the solid crystal. Gas phase data have been absent, probably due to difficulties in detection of the weak fluorescence [4]. We here present our initial results on a gas phase two-photon spectrum of pyrazine.

Pyrazine has been studied extensively by one-photon UV absorption by a number of groups [5 – 7]. In the vapour phase investigations of the lowest state of pyrazine ($\pi^* \leftarrow n$, $^1B_{3u}$, axes convention after Ref. [5]). Ito et al. [6] found that the absorption spectrum consists of a narrow and a broad system the origin of which was not identified. Innes et al. [7] showed by high resolution vapour spectroscopy of these systems and their extensive rotational contour calculations that both band systems belong to one electronic transition ($^1B_{3u}$), but the sharp bands are electronically allowed transitions (0-0 transition: 30875.8 cm^{-1}) with their transition moment perpendicular to the plane of the molecule (C-type) while the broad bands show in-plane polarization along the y-axis (B-type) of the molecule. Only one vibration, namely the out-of-plane hydrogen-bending mode ν_{10a} (b_{1g}) was proposed to couple the $^1B_{3u}$ ($\pi^* \leftarrow n$) state to the $^1B_{2u}$ ($\pi^* \leftarrow \pi$) state, and in this way the transition gains intensity by vibronic interaction [7].

In this paper we wish to present new spectroscopic results about the vibrational structure of the $^1B_{3u}$ state. This spectroscopic information is obtained by a two-photon excitation of this state and is due to the different selection rules for an electric dipole transition. A pure electronic two-photon transition to the $^1B_{3u}$ state is not possible because of the parity selection rule. Thus only transitions induced by vibrations of u-parity (a_u, b_{1u}, b_{2u}, b_{3u}) can be expected in a two-photon spectrum of this electronic state $^1B_{3u}$ in a point group D_{2h}.

The experimental setup for measuring the two-photon excitation spectrum of pyrazine in the gas phase principally is the same as in [8].

We used a nitrogen pumped dye laser (Molectron UV 24, DL 14 P) with a peak power of some 90 kW (Rb B) and a bandwidth of 0.6 cm^{-1} at 6200 Å. The wavelength was calibrated directly against the lines of a neon spectral lamp and monitored by a spectrometer (1.5 m, Jobin Yvon THRP) with an adapted optical multichannel analyzer mounted in the exit plane.

The accuracy of the given band positions is ± 1 cm^{-1}. The vapour pressure of pyrazine at 20 °C is 7 torr. In order to obtain higher fluorescence intensities in some parts of the experiments the gas cell was heated to achieve a vapour pressure of about 60 torr. Before filling the cell the pyrazine samples (pyrazine-h_4, Merck-Schuchardt, 99% purity; pyrazine-d_4, Merck, Sharp and Dohme, 98 atom% D) were outgassed thoroughly and vacuum sublimed.

In Fig. 1 a low resolution two-photon spectrum between 30 000 cm^{-1} and 32 600 cm^{-1} is shown. The intensity is sufficient to observe some features in the hot band region to the red of the parity forbidden $^1B_{3u} \leftarrow {}^1A_g$ two-photon transition.

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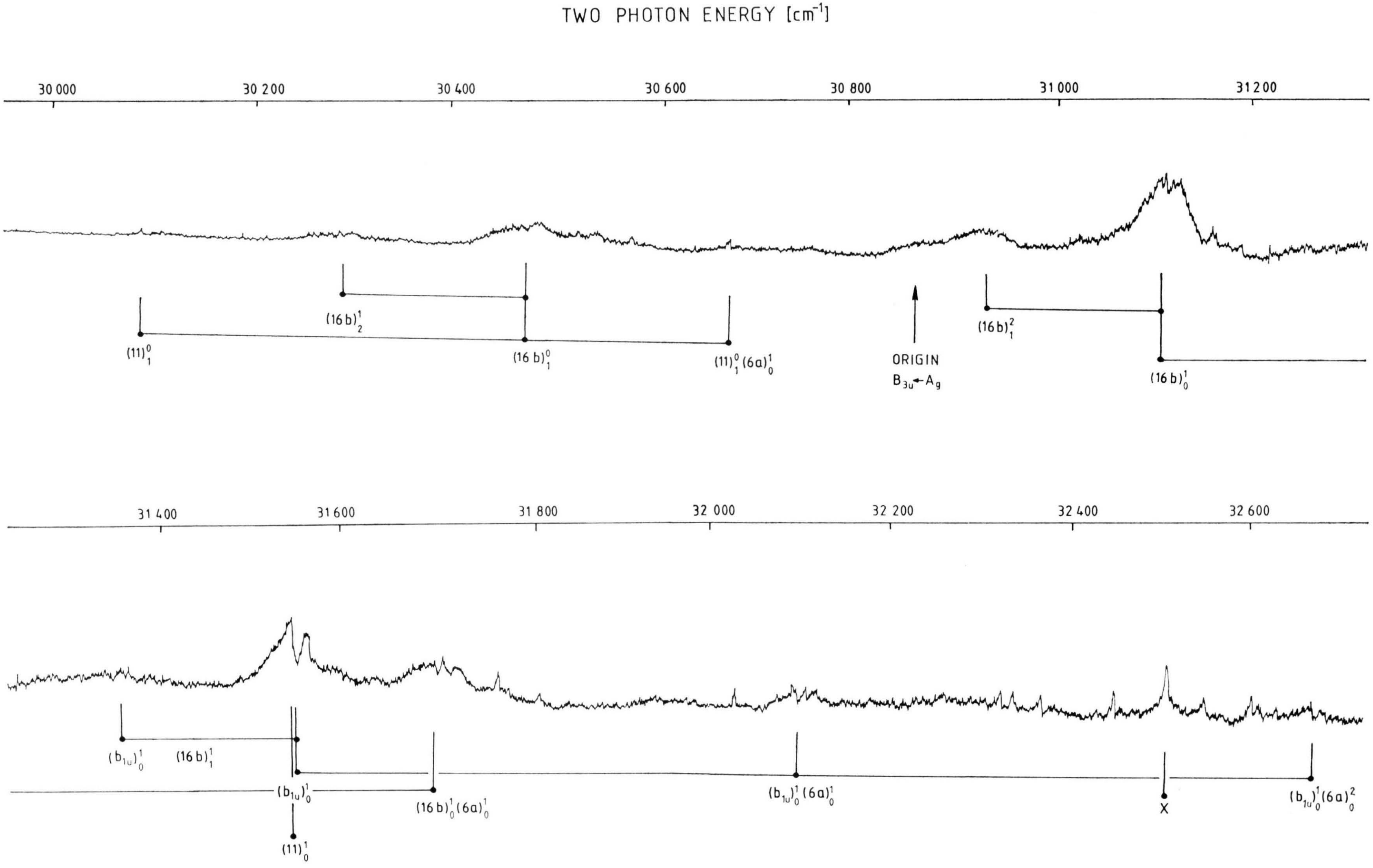

Fig. 1. Two-photon excitation spectrum of gas phase pyrazine-h$_4$ under low resolution. The pure electronic $S_1 \leftarrow S_0$ transition is parity forbidden and the two-photon transition is vibrationally induced.

Four types of bands can be classified in the spectrum from the general rotational band structure and their polarization behaviour:

i) Broad totally symmetric bands with only a very small isotropic part which disappears in going from linear to circular polarized light [9] whereas the large anisotropic part of the bands is enhanced in its intensity. The polarization ratio $R^{\updownarrow\updownarrow/\circlearrowleft\circlearrowleft}$ of the integrated band area is 0.73 for the fundamental at 31 111 cm^{-1}. This ratio $R^{\updownarrow\updownarrow/\circlearrowleft\circlearrowleft} = 0.73$ is very close to $R^{\updownarrow\updownarrow/\circlearrowleft\circlearrowleft} = 2/3$ typical for a non-totally symmetric two-photon transition [10]. Therefore it was difficult to identify the band as due to a totally symmetric two-photon transition. This has been achieved only by a comparison with asymmetric rotor calculation [11]. In the spectrum of pyrazine-h$_4$ we found one fundamental band of this type at 235 cm^{-1} above the origin and at 416 cm^{-1} below the origin. From the hot band frequency [12] we were able to assign it as due to the inducing vibration $16\,b_0^1$ of b_{3u} symmetry. $16\,b_0^1$ and $16\,b_1^0$ show a sequence band at about 180 cm^{-1} to the red which is due to the same vibration. No long progression sequences of an a_g vibration were observed. For pyrazine-d$_4$ we found 213 cm^{-1} and 398 cm^{-1} for $16\,b_0^1$ and $16\,b_1^0$ [12, 13], respectively, with the sequence band at about 185 cm^{-1} to the red. This vibration has been found by Esherick et al. [3] in their two-photon excitation spectrum of the low temperature pyrazine-h$_4$ crystal at the different frequency of 263 cm^{-1}.

ii) One double-headed band without an isotropic contribution with a sequence band 180 cm^{-1} to the red. In the spectrum of pyrazine-h$_4$ there is an accidental overlap between bands of type ii) and iii). From asymmetric rotor calculations the symmetry of this inducing mode is found to be b_{1u}, the band origin was determined to be 647 cm^{-1} and 616 cm^{-1} in pyrazine-h$_4$ and -d$_4$, respectively. This band is either $18\,a_0^1$ or 12_0^1 [13]. In pyrazine-h$_4$ at 1225 cm^{-1} there is an overlap of the progression in $6\,a_0^1$ with the progression in 1_0^1 [5] of the $16\,b_0^1$ fundamental.

iii) Sharp totally symmetric peaks placed on a broad background. No sequence bands could be resolved. As mentioned in ii) one of these bands is hidden by the b_{1u} band in the pyrazine-h$_4$ spectrum. The frequencies taken at the maximum of the totally symmetric part of the bands are 639 cm^{-1} and 533 cm^{-1} for pyrazine-h$_4$ and -d$_4$, respectively. In the hot band region we found similarly shaped bands at 786 cm^{-1} (-h$_4$) and 597 cm^{-1} (-d$_4$). These frequencies correspond well to the known ground state frequencies of 11_1^0, the second b_{3u} vibration [13]. This is a direct confirmation of the frequency of this band found as a doubly excited band by Narva et al. [14].

iv) Sharp and strong totally symmetric bands (e. g. at 32 507 cm^{-1}) with a small anisotropic part. These bands are not found to show any sequence bands. In the pyrazine-d$_4$ spectrum there is only one like band which is the most intense of the whole spectrum. Further work on the origin of these bands based on rotational band contour calculation is in progress.

All observed vibrational frequencies are put together in Table 1. We are able to identify 3 frequencies of the S_1-state in pyrazine-h$_4$ and -d$_4$ complementary to the vibrational frequencies known from one-photon spectra. Detailed work on the rotational analysis of these bands is in progress [15].

Table 1. The vibrational frequencies of pyrazine-h$_4$ and (-d$_4$) as determined from the gas phase two-photon spectrum. All band intensities are normalized to the strongest band induced by ν_{16b} in pyrazine-h$_4$.

Vibration	Vibrational symmetry	Frequencies (cm^{-1}) in ^1A_g ground state	Frequencies (cm^{-1}) in $^1B_{3u}$ excited state	Normalized intensities
16 b	b_{3u}	416 (398)	235 (213)	100 (112)
11	b_{3u}	786 (597)	639 (533)	25 (26)
18 a or 12	b_{1u}		647 (616)	80 (82)

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