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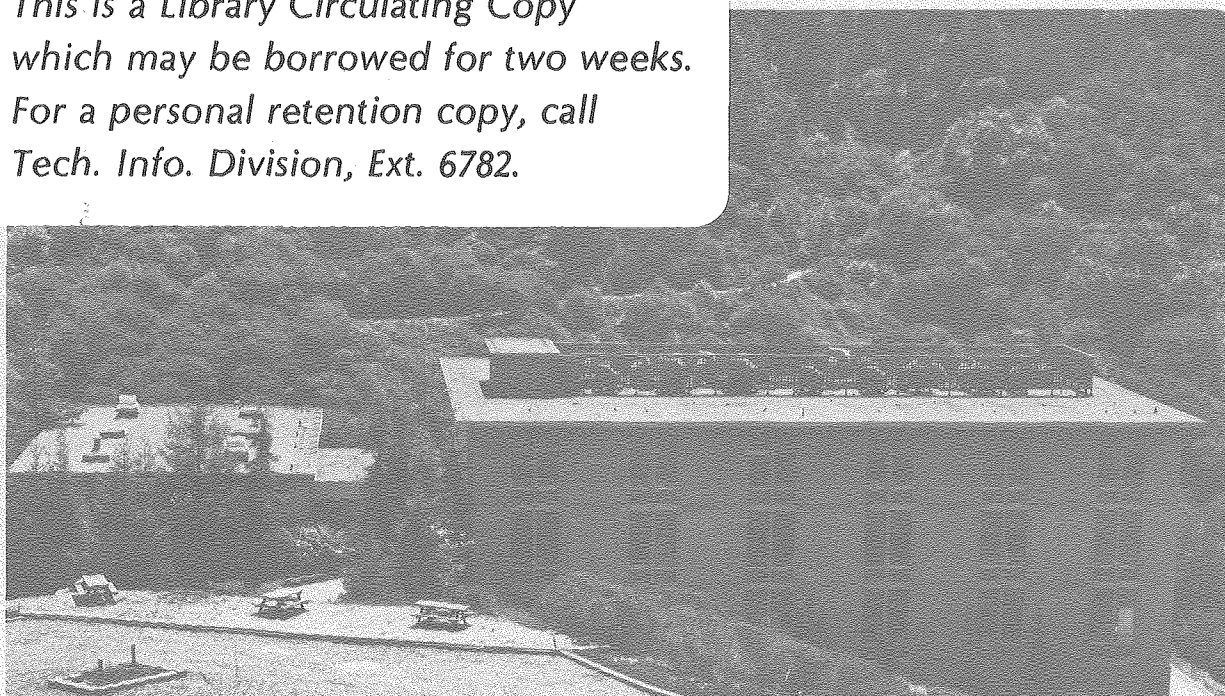
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The Laser Induced Fluorescence Spectrum of Trapped BrCN Cations

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Abstract

Laser induced fluorescence spectra of mass selected BrCN^+ confined in a three dimensional quadrupole trap are presented. Using this technique, the $\tilde{B}^2\Pi-\tilde{X}^2\Pi$ system of BrCN^+ is investigated. Approximate values for the C-Br stretching frequencies ($\nu_1' = 441 \pm 18 \text{ cm}^{-1}$, $\nu_1'' = 509 \pm 16 \text{ cm}^{-1}$) and the difference of the spin-orbit splitting constants ($A''-A' = 224 \pm 43 \text{ cm}^{-1}$) are determined. However, the spectrum is complicated by irregular vibrational and spin-orbit splitting spacing yielding a large uncertainty in these values. The existence of sequence bands and a Fermi resonance interaction provide possible explanations for these irregularities.

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Introduction

In 1970, Herzberg pointed out that, in the case of molecular ions, spectroscopic information has been very limited.¹ Since that time, the optical spectra of many molecular ions have been observed.^{2,3} The emission spectra of several molecular ions have been obtained by Maier and co-workers using a controlled electron impact technique.³ One such example is the spectra of several halocyanide cations observed by Allan and Maier.⁴ In the particular case of BrCN^+ , they were able to assign some of the vibrational bands in the $\tilde{A}^2\Sigma-\tilde{X}^2\Pi$ spectrum, but were unable to make specific band assignments in the $\tilde{B}^2\Pi-\tilde{X}^2\Pi$ system.

We undertook the study of BrCN^+ with a new experimental technique in the hopes of obtaining information concerning the vibrational structure and spin orbit coupling in the $\tilde{B}-\tilde{X}$ system. Our technique combines the use of three dimensional quadrupole trapping and laser induced fluorescence (LIF) to produce fluorescence excitation spectra of molecular ions. The ion trap confines a reasonably high density of ions in a region easily probed by a laser beam and also allows mass selection which serves to isolate and identify the ions desired for study. The trap also permits experiments to be operated at very low pressures, nearly eliminating collisions and thus preserving the initial ion ro-vibrational state distribution.⁵ In many cases, this will allow spectral information to be obtained about the ground electronic state as well as the excited electronic state. However, in some cases, as is seen for BrCN^+ , the vibrational state distribution in the ground electronic level of the ion spans several quantum levels leading to a situation in which some spectral detail is obscured due to overlapping hot band sequences.

Experimental

The three dimensional quadrupole ion trap chosen for our work was of cylindrical geometry⁶ rather than the typical hyperbolic geometry.⁷ The trap consists of a hollow cylindrical center electrode and two flat wire-mesh electrodes, one at each open end of the cylinder. The cylindrical configuration was selected in order to minimize the distortion of the electric fields due to the holes that were cut in the center electrode to allow for passage of the laser and electron beams. The ions are created in the center of the trap by electron bombardment of the parent neutral gas from a pulsed electron gun mounted on the center electrode. It was necessary to include a shield and baffle system inside the electron gun to diminish background light produced by the hot thoriated tungsten filament.

The ions are trapped by applying a radio frequency electric field with a dc bias to the center electrode and keeping the end cap electrodes at ground. By varying the ratio of the dc bias to the radio frequency potential, a variable mass resolution can be obtained.⁸ When it is necessary to isolate the ions of interest from ions possessing a similar charge to mass ratio, the ions are confined using high mass resolution. We used the ion trap in such a manner recently⁵ to obtain a spectrum of CD^+ . When such isolation is not required, low mass resolution is utilized, which increases the concentration of the ions in the trap and thereby increases the signal intensity. The trap was used in this low bias mode to obtain the BrCN^+ spectrum presented in this paper. At a pressure of $10^{-4} - 10^{-6}$ torr of neutral gas an estimated density of $10^6 - 10^8$ ions cm^{-3} is obtained in a few milliseconds and can be stored for tens of milliseconds.

Although the trapping potential operates continuously, the remainder of the experiment is operated in a pulsed mode at a repetition rate of 10-40 Hz. The experiment is most easily described by considering one experimental cycle, which consists of three parts: ion creation and confinement, excitation of the ions, and fluorescence signal detection. A schematic of our experiment is given in Fig. 1 to aid in this discussion.

The experiment begins with the initiation of the electron beam that creates ions for a period of 1-20 msec. The electron gun is then gated off and a delay period of ~ 1 millisecond ensues. During this time any necessary mass selection of the ions is allowed to occur and any excited electronic states that have been created are permitted to relax radiatively. After the delay period, a 10 nsec, 1 cm^{-1} bandwidth laser pulse from a Molelectron DL-200 dye laser pumped by a UV-1000 nitrogen laser is passed through the ion cloud. The 1 cm^{-1} band width of the laser matches the expected Doppler linewidth of the trapped ions. Any subsequent fluorescence is then monitored at right angles to the laser beam. A lens and mirror system with an estimated 10% collection efficiency directs any fluorescence which passes through wire-mesh end electrodes to a "naked" RCA 8575 photomultiplier tube (PMT). The PMT signal is gathered by a gated photon counting system.

In addition to fluorescence, scattered laser light may also reach the detection system. In order to minimize this background radiation, the laser beam is collimated to about 0.5 cm diameter with two lenses and directed through 0.5 meter arms containing light baffles on the entry and exit side of the trap.⁹ In addition to the baffle system the short laser pulse allows the use of gated detection techniques to reduce the effects of scattered laser light. The PMT was used with a gated

dynode chain¹⁰ in order to keep the PMT at low gain during the time of the laser pulse. A signal from a photodiode detecting the laser light triggers the dynode chain to switch to high gain shortly after the passage of the laser light. A change in gain of 100 can be accomplished in about 50 nsec with very little signal ringing or jitter.⁹

The signal from the photodiode also triggers the beginning of a fluorescence detection gate. The initiation of this gate can be variably delayed with respect to the laser pulse and its duration can also be varied between 0.1 and 10 μ sec. The duration of the gate is primarily determined by the radiative lifetime of the ionic species being investigated. The fluorescence detection gate and the signal from the PMT are sent to a gated single photon counting system which consists of an L.R.S. 621-BL discriminator and an Ortec 770 100 MHz counter.

After the fluorescence detection, the experimental cycle is completed by pulsing the ions out of the trap to a magnetic electron multiplier. In order to get a consistent ion signal from cycle to cycle a high voltage pulse that is synchronized with the r.f. trapping potential must be applied to the bottom trap electrode. The signal is measured by an L.R.S. 227-sg integrator and is used to normalize the fluorescence signal. The laser power, which is measured by a photodiode and the L.R.S. 227-sg integrator, is also used to normalize the fluorescence signal. The final signal gathered by the integrator is used to calibrate the laser wavelength. Calibration is accomplished by shining the laser into a hollow-cathode discharge lamp containing Ne and measuring metastable Ne transitions by the optogalvanic effect.¹¹

An on-line PDP-8f computer is responsible for the overall control of the experiment. At the end of an experimental cycle, the computer

gathers the signals from the integrator and initiates a new cycle. After a predetermined number of cycles (or laser shots) the computer retrieves the fluorescence signal from the counter and advances the laser wavelength by a preset increment. Typically the signal is averaged over about a thousand laser pulses before advancing the wavelength. The computer normalizes the data, stores it on floppy disk, and produces a hard copy of the spectrum.

The specific conditions under which the BrCN^+ experiments were performed are the following. The BrCN pressure was kept at $3\text{--}5 \times 10^{-5}$ torr. Because no interfering ions were produced, low mass resolution conditions (± 10 a.m.u.) were used. To monitor the fluorescence from the $\tilde{\text{B}}$ state (which has a radiative lifetime of 270 nsec)⁴ a detection gate 2 μsec in duration beginning 200 nsec after the laser pulse was found to be optimum. Because the rotational spacing in BrCN^+ is too small to be resolved in our experiment, a $0.5 \text{ \AA}$ wavelength increment was used, allowing the observation of vibrational structure. The appearance of the spectrum did not change when a smaller wavelength increment was used. The fluorescence signal at each wavelength was averaged over 750 laser shots.

Results

The fluorescence excitation spectrum we observed for the $\tilde{\text{B}}\text{--}\tilde{\text{X}}$ transition of BrCN^+ is reproduced in Fig. 2. A vibrational progression with an average frequency of $441 \pm 18 \text{ cm}^{-1}$ is observed. By comparison with results from photoelectron spectroscopy¹² and the infrared spectrum¹³ of BrCN , this progression can be assigned to the ν_1 vibrational mode of the $\tilde{\text{B}}$ electronic state. This mode consists primarily of the C-Br stretching motion. The average value we obtain for the frequency of this mode is somewhat lower than the 516 cm^{-1} found in the photoelectron

spectrum. The photoelectron results^{4,12} also indicate that a long progression in this mode is expected in our spectrum with a band origin at 18601 cm^{-1} . As can be seen in Fig. 2, a long progression does occur, but no transitions in the vicinity of 18600 cm^{-1} are observed. The non-appearance of the 0_0^0 band is not surprising, since the photoelectron spectrum¹² indicates that the Franck-Condon factor for this band is expected to be small. The v_1' vibrational quantum numbers are assigned assuming that the band origin is at 18601 cm^{-1} . The assignment shown in Fig. 2 should, therefore, be considered tentative. The band positions, differences, and assignments are given in Table 1.

The discrepancy between our value ($v_1 = 441 \text{ cm}^{-1}$) and the photoelectron spectroscopy value ($v_1 = 516 \text{ cm}^{-1}$) can be partly explained by the long progression seen in the $\tilde{B}-\tilde{X}$ spectrum. Because we are observing transitions to higher v_1 levels than in PES, our value would be expected to be somewhat lower due to anharmonicity. Another explanation for the differences stems from the uncertainties in both values. The uncertainty in our value is primarily due to the irregular vibrational spacing which occurs in our spectrum. As can be seen in Table 1, v_1' varies between 402 cm^{-1} and 481 cm^{-1} . Possible explanations of this irregular spacing are discussed later.

Each of the vibrational bands shown in Fig. 2 is seen to consist of four peaks. The splitting of $\Omega = 3/2$ and $\Omega = 1/2$ states has been shown^{4,12} to be large for both the $\tilde{X}$ and $\tilde{B}^2\Pi$ electronic states, being $A'' = -1470 \text{ cm}^{-1}$ and $A' \approx -1200 \text{ cm}^{-1}$. Because only the $^2\Pi_{3/2} - ^2\Pi_{3/2}$ and $^2\Pi_{1/2} - ^2\Pi_{1/2}$ transitions are allowed due to the $\Delta\Sigma = 0$ selection rule for a transition between Π states belonging to Hund's case (a), our vibrational bands would be expected to split into two subbands. The separation of

these subbands represents an approximation to the difference in spin-orbit coupling constants of the two electronic states, $\Delta A = A'' - A'$.

The ΔA values obtained in our spectrum are given in Table 2, where an average value of $\Delta A = 224 \pm 43 \text{ cm}^{-1}$ is determined. The large uncertainty is again due to a nonsystematic spacing from band to band.

The fact that each Ω subband consists of two peaks may offer a clue as to why we are observing irregular spacings in our spectrum. The additional peaks are believed to be hot bands differing from their neighboring bands by one quanta in both v_1' and v_1'' . The frequencies of these hot bands are given in Table 1 in the columns labeled $(v_1'' + 1)$. Using only the better resolved $\Omega = 3/2$ component of each vibrational band, we find a difference between the v_1 vibrational frequencies of the $\tilde{X}$ and the $\tilde{B}$ electronic states of $\Delta v_1 = v_1'' - v_1' = 68 \pm 10 \text{ cm}^{-1}$. This compares well with a difference of 64 cm^{-1} obtained from the photoelectron spectrum⁹ lending support to the assignment of these extra peaks as hot bands. This frequency difference results in an $\tilde{X}$ state stretching frequency of $v_1'' = 509 \text{ cm}^{-1}$, which is again lower than the value obtained from photoelectron spectroscopy, 575 cm^{-1} .

This assignment suggests that our ion sample is vibrationally and perhaps rotationally "hot". An excited vibrational ion sample is certainly expected when spectra previously obtained for BrCN^+ and our method of ion production are considered. The photoelectron spectrum^{4,12} shows considerable electronic and vibrational excitation in the formation of BrCN^+ . The emission spectra obtained by electron impact⁴ also indicate that cascading from the $\tilde{B}$ and $\tilde{A}$ electronic states into excited levels of each vibrational mode of the $\tilde{X}$ state is highly probable. Our ions, also created by electron impact, are then expected to be vibrationally hot.

Furthermore, because we operate at a low pressure (10^{-5} torr) very few thermalizing collisions (~ 1 collision/msec) will occur before the interaction of the ion sample with the laser light.

In addition to the apparent hot bands we observe, the conditions described above would also be expected to result in the appearance of sequence bands in our spectrum. We believe that sequence bands coupled with our low resolution are responsible for the pseudocontinuum seen in Fig. 2. It is also believed that, if there is considerable vibrational excitation in the initial state of our ion sample, sequence bands could explain the irregular vibrational spacing, spin-orbit splitting, and intensities in our spectrum. The overlap of numerous sequence bands could account for the apparent band shifts that we observe. It is also possible, depending on the difference in the molecular constants of the $\tilde{X}$ and $\tilde{B}$ states, that sequence heads occur in our spectrum with their relative positions varying from band to band. Because of the appearance of sequence bands, we have not assigned absolute vibrational quantum numbers to our spectrum. Rather, the bands in Fig. 2 and the frequencies in Table 1 are labeled by a difference in the v_1 quantum numbers between the two electronic states, $\Delta v_1 = v_1' - v_1''$, assuming a band origin at 18601 cm^{-1} .

There is, however, an additional interaction that might account for the irregularities occurring in our spectrum. In many symmetric¹⁴ and nonsymmetric¹⁵ linear triatomic molecules, where the bending vibrational frequency is approximately half the magnitude of one of the stretching vibrational frequencies, a Fermi resonance interaction has been found to occur. In fact, one such example is the neutral BrCN molecule.¹³ This interaction has been shown to result in band shifts

and considerable intensity borrowing by otherwise weak ν_2 quanta (ν_2 even) transitions.

It is highly probable that a Fermi interaction occurs in both the $\tilde{B}$ and $\tilde{X}$ electronic states of BrCN when the approximate vibrational frequencies are considered. The bending frequency for the $\tilde{X}$ state has been estimated from the $\tilde{A}$ - $\tilde{X}$ emission spectrum^{4,16} to be about 290 cm^{-1} and is not expected to vary substantially from this value in the $\tilde{B}$ state. When this bending frequency is compared with the stretching frequencies, $\nu_1' = 441\text{ cm}^{-1}$ and $\nu_1'' = 509\text{ cm}^{-1}$, a Fermi interaction does indeed seem plausible. An alternative explanation of our spectrum would then be that the extra peak observed in each subband is a transition involving Fermi resonant levels. The nonsystematic spacings and irregular intensities observed would result from the variance in the magnitude of the Fermi interaction from band to band.

Most likely, both a Fermi resonance interaction and the existence of sequence bands are playing a role in the observed $\text{BrCN}^+ \tilde{B}$ - $\tilde{X}$ spectrum. The next step would be a modeling of the spectrum including all the effects which are believed to be present. However, the present resolution and the fact that no unperturbed bands were observed preclude such an analysis. We are planning experiments with collisionally relaxed BrCN^+ in order to obtain a simplified LIF spectrum. We hope this will allow a modeling of the spectrum to determine the extent of the Fermi resonance interaction and the effect of sequence bands in our spectrum.

Conclusion

The laser induced fluorescence spectrum of the $\tilde{B}$ - $\tilde{X}$ transition of BrCN^+ has been obtained. From the spectrum a C-Br stretching frequency was determined for the $\tilde{B}$ state, $\nu_1' = 441 \pm 18\text{ cm}^{-1}$, and the $\tilde{X}$ state,

$\nu_1'' = 509 \pm 16 \text{ cm}^{-1}$. An approximation to the difference in the spin orbit splitting constants between these two states was also found. $\Delta A = 224 \pm 43 \text{ cm}^{-1}$. Irregular vibrational and spin-orbit spacings were observed in the spectrum, and a first order explanation involving sequence bands was suggested. The agreement between $\nu_1 (= \nu_1'' - \nu_1')$ values in our spectrum and in PES supports this interpretation. It was also pointed out that another interaction, Fermi resonance, is most likely involved in this spectrum and should also be considered as another source of the observed band shifts and irregular intensities.

Acknowledgements

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Table 1. Frequencies and assignments of subband heads for the $\tilde{B}^2\Pi - \tilde{X}^2\Pi$ transition of BrCN^+ frequency differences between bands are given in parenthesis. $\Delta v_1 (= v_1' - v_1'')$ quantum number assigned assuming 18601 cm^{-1} as band origin. $\Delta v_1 = v_1'' - v_1'$. All frequencies are in cm^{-1} and have not been corrected to vacuum.

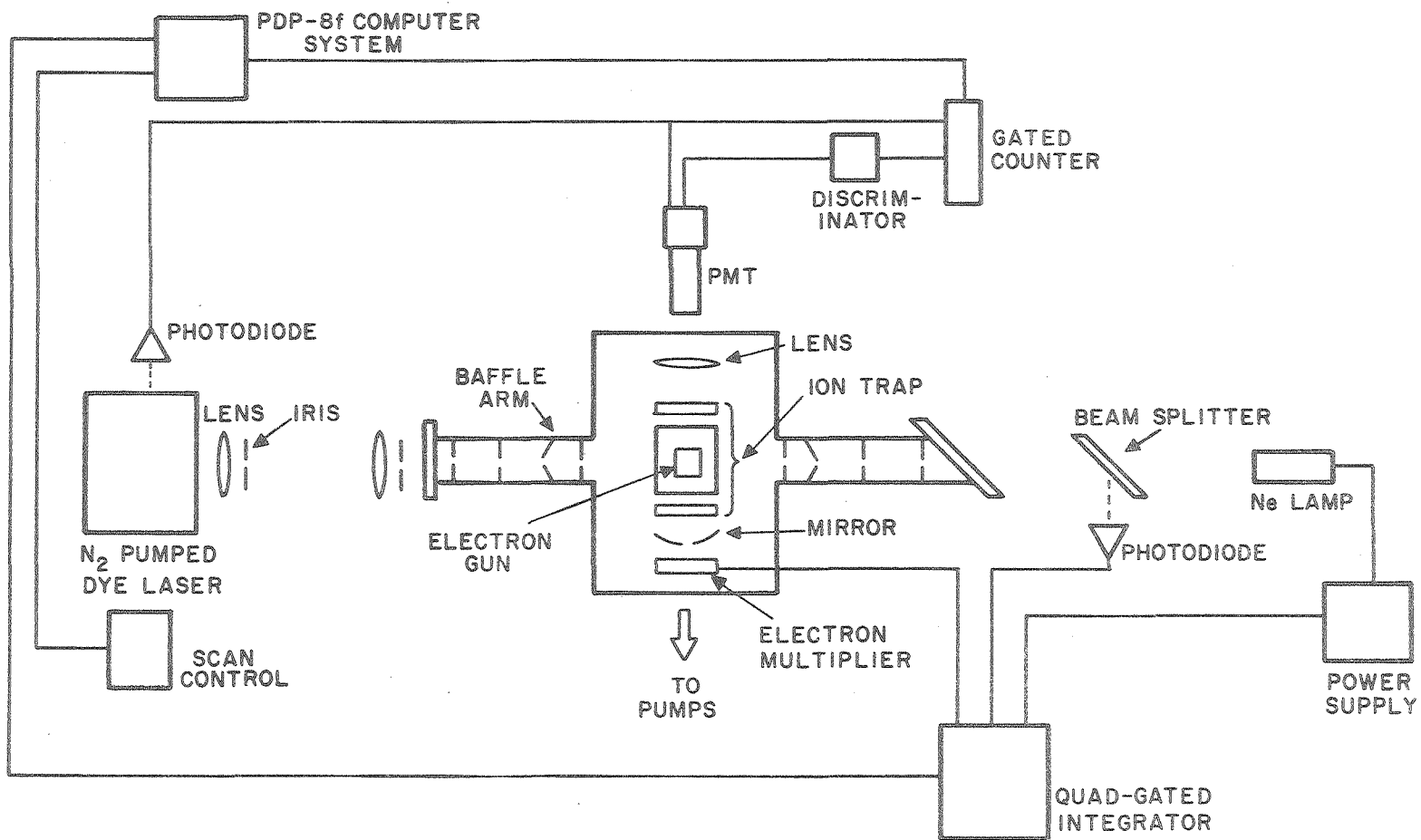
$^2\Pi_{3/2} - ^2\Pi_{3/2}$				$^2\Pi_{1/2} - ^2\Pi_{1/2}$	
Δv_1	$\bar{\nu}(v_1'')$	Δv_1	$\bar{\nu}(v_1'' + 1)$	$\bar{\nu}(v_1'')$	$\bar{\nu}(v_1'' + 1)$
4	20537	(55)	20482	20275	20205
v_1'	(463)		(455)	(449)	(426)
5	21000	(63)	20937	20724	20631
v_1'	(466)		(450)	(450)	
6	21466	(79)	21387	21174	—
v_1'	(402)		(421)	(466)	
7	21868	(60)	21808	21640	21592*
v_1'	(454)		(442)	(481)	(449)
8	22322*	(72)	22250	22121	22041*
v_1'	(431)		(433)	(447)	(443)
9	22753	(70)	22683	22568	22484
v_1'	(434)		(424)	(447)	(438)
10	23187	(80)	23107	23015*	22922*
v_1'			(441)		(441)
11			23548*		23363*
v_1'			(416)		(407)
12			23964		23770*
v_1'			(443)		(432)
13			24407		24202

* The uncertainty in these frequencies is $\pm 20 \text{ cm}^{-1}$. All of the others are $\leq \pm 10 \text{ cm}^{-1}$.

Table 2. Approximate spin-orbit
coupling constant dif-
ferences in cm^{-1} .
 $\Delta A = A'' - A'$.

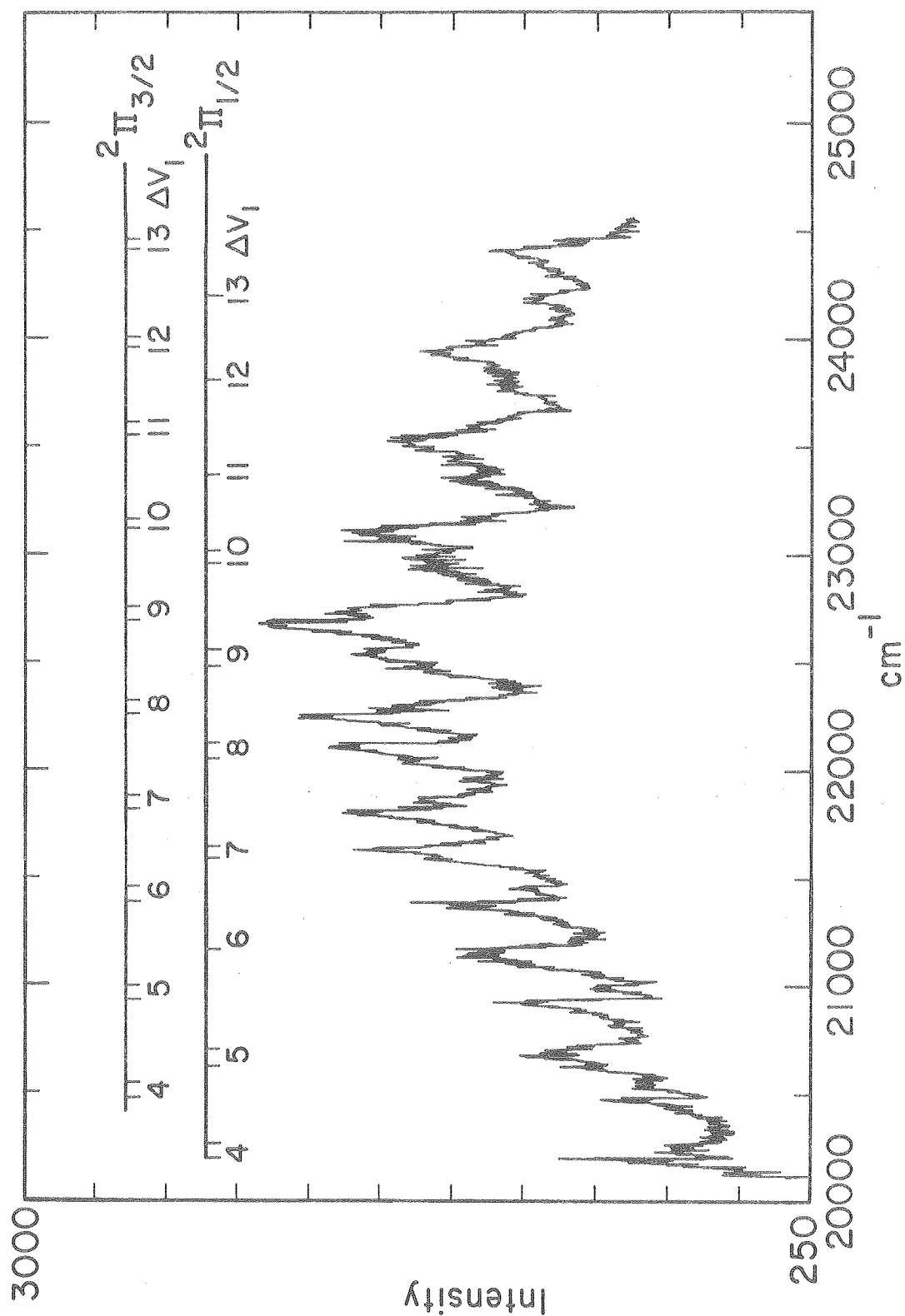
Δv_1	$\Delta A(v_1'')$	$\Delta A(v_1'' + 1)$
4	262	277
5	276	306
6	292	-
7	228	210
8	201	209
9	185	199
10	172	185
11	-	185
12	-	194
13	-	205

Figure 1. Schematic representation of the experiment.



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Figure 2. Fluorescence Excitation Spectrum of BrCN^+ : $\tilde{\text{B}}^2\Pi - \tilde{\text{X}}^2\Pi$ Band System. The quantum numbers are assigned with the assumption that the band origin occurs at 18601 cm^{-1} .
 $\Delta v_1 = v_1' - v_1''$.



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