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# A new band system of nitrogen: Observation of the $N_2(G^3\Delta_g \rightarrow W^3\Delta_u)$ transition

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The first experimental observation of the  $N_2(G^3\Delta_g \rightarrow W^3\Delta_u)$  transition is reported on here. The emission forms part of the spectrum of the so-called  $N_2$  beam afterglow, a spontaneous luminescence emitted by a molecular beam of  $N_2$  issuing from an intense d.c. discharge. Using a high performance charge-coupled device (CCD) optical multichannel detector, 18 bands of a new band system were observed with 2 Å full width at half-maximum (FWHM) resolution in the 350–650 nm region. Three well-resolved  $v''$  progressions were analyzed. From a comparison with the known vibrational spacings in the  $N_2(G)$  and  $N_2(W)$  states, they could be assigned unambiguously to the  $N_2(G \rightarrow W)$  transition. This observation allows the energy of the  $N_2(G)$  state to be determined as  $T_e = 89\,505\text{ cm}^{-1}$  or 11.10 eV, thereby also fixing the location of the previously observed  $H(^3\Phi_u)$  state at  $T_e = 107\,328\text{ cm}^{-1}$  or 13.31 eV.

## I. INTRODUCTION

In spite of the fact that  $N_2$  is one of the best studied molecules,<sup>1,2</sup> the positions of some of its excited states on the energy scale are still poorly known. Two examples are the higher  $N_2$  triplet states  $H$  and  $G$ . The transition between these two states is known as the Gaydon–Herman green system and has long been observed in discharges or by means of electron beam excitation.<sup>3–7</sup> In the first high resolution study,<sup>8</sup> this system was identified as the  $H^3\Phi_u \rightarrow G^3\Delta_g$  transition. Subsequently, a more refined rotational analysis of the  $H$  and  $G$  states was done.<sup>9</sup> The location of both these states relative to the rest of the  $N_2$  triplet states, however, remained uncertain. An estimate of  $T_e$  for the  $G$  state was obtained in Ref. 8 from a Birge–Sponer extrapolation to the expected dissociation limit  $N(^4S) + N(^2D)$ , with the result of  $T_e = 87\,150\text{ cm}^{-1}$  corresponding to 10.8 eV. *Ab initio* calculations<sup>10–12</sup> place the  $G$  state at an energy  $\sim 11$  eV.

In Ref. 13, an attempt was made to observe laser-induced fluorescence (LIF) from the  $G$  state under flow system conditions via its excitation in the dipole allowed transition  $G^3\Delta_g \leftarrow W^3\Delta_u$ . However, no  $G \rightarrow W$  fluorescence signal in the range 400–600 nm was detected when scanning the probe laser from 375 to 400 nm. For an explanation, the authors referred to unpublished results of Alexander and Werner, where it was suggested that due to a special type of the  $\pi_u^2\sigma_g^2\pi_g^2$  electronic configuration of the  $G$  state, the oscillator strength of the  $G \rightarrow W$  transition should be quite small. A related and probably more important reason for the failure to observe LIF is that the  $N_2(G)$  molecules, even if laser excited, are likely to be quenched in the collisional environment due to their long radiative lifetime. Another complexity arising in the conventional discharge excitation is the overlap of the  $G$ – $W$  spectrum with other nitrogen transitions in the same spectral region. The

molecular beam afterglow, on the other hand, is ideally suited for the observation of this system because it permits a separation of transitions from the long-lived and the short-lived states via the time of flight under collision-free conditions. In this work, we report on the first observation of the  $G \rightarrow W$  transition made in the beam afterglow.

## II. EXPERIMENT

The experimental arrangement used in this work has been described in detail in Refs. 14–18. A collimated supersonic beam of excited nitrogen molecules is generated by means of a d.c. discharge in the beam expansion region. Spontaneous emission from the beam is observed through optics which can be placed at distances of 23–70 cm from the discharge. The observation point was shielded against stray light from the discharge by means of a blackened cell surrounding the beam (entrance and exit diaphragms 5 mm diameter). This cell had originally been installed to serve as a target gas cell for collision experiments.<sup>17,18</sup> In the present work, the cell was usually empty, except for some auxiliary experiments (see below).

The main difference from the previous beam afterglow study<sup>15</sup> was the use of a new high performance charge-coupled device (CCD) array detector system for spectral measurements. Light originating from the beam was observed through a quartz window sealed on top of the collision cell. It was collected by a high-grade UV quartz fiber bundle with a 50 mm<sup>2</sup> cross section (Instruments S.A.) and was conducted to a 0.25 m Chromex model 250IS spectrograph equipped with 2400, 1200, and 600 mm<sup>−1</sup> gratings. Second-order signals of short-UV emission were eliminated by a BK-7 glass filter. This proved to be very important because the  $N_2$  beam afterglow contained a rather strong  $a^1\Pi_g$ ,  $v' = 2-6 \rightarrow X^1\Sigma_g^+$  Lyman–Birge–Hopfield component, which interfered severely in second order with the measurements in the 380–450 nm region. The spectra were recorded by a liquid-nitrogen cooled CCD camera (Wright Instruments Ltd., model 1) attached directly to the spectrograph. The detector chip

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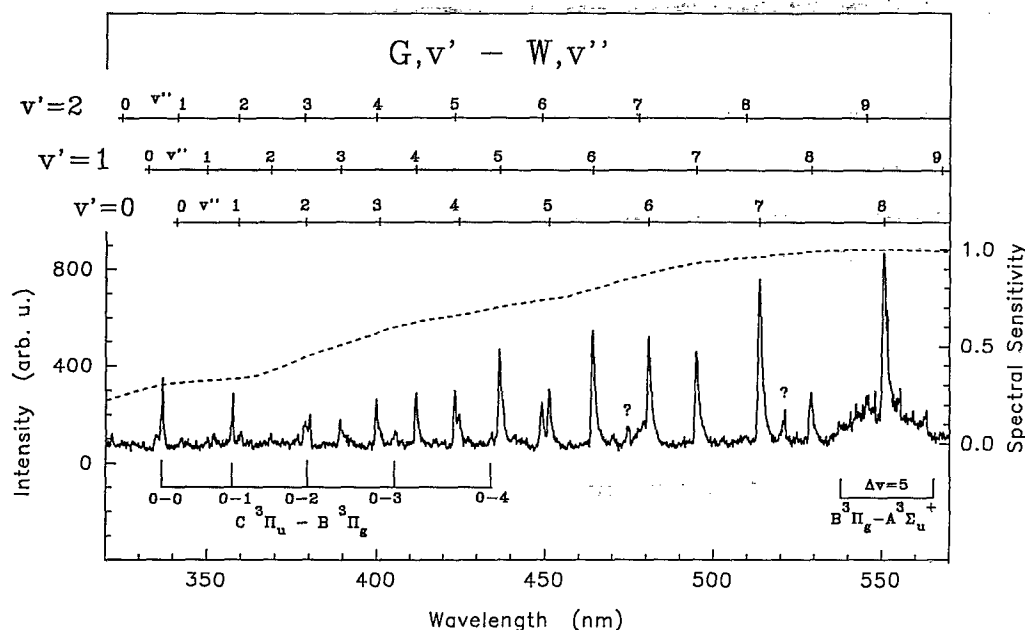


FIG. 1. A typical spectrum of the beam afterglow. Spectral resolution is 0.3 nm FWHM. The intensities are uncorrected for the relative spectral sensitivity of the detection system, which is shown as a dotted line. The spectrum is a composite of ten adjacent sections recorded separately with exposure times of  $10 \times 200$  s each (i.e., entire data collection time  $\approx 5.5$  h). The base level of 65 arbitrary units is given by the read-out noise. The newly discovered  $N_2(G \rightarrow W)$  bands are labeled at the top; some additional  $N_2(C \rightarrow B)$  and  $N_2(B \rightarrow A)$  bands are marked at the bottom.

(EEV type 02-06-1-206) contains 550 usable rows of pixels, each  $22 \mu\text{m} \times 22 \mu\text{m}$  in size. It is of the back-illuminated type with a coating for enhanced UV sensitivity. On-chip binning of the 385 usable pixels in each row was employed. Cosmic-ray background peaks in the spectra were eliminated by appropriate software. It was necessary to perform this procedure periodically every 200 s to avoid an excessive amount of obliteration of the true signals. After each cosmic ray peak subtraction, the data accumulation was continued until a satisfactory signal-to-noise (S/N) level was reached. A typical exposure time was  $10 \times 200$  s. The spectrograph/CCD combination used permits spectral sections 15, 30, and 60 nm wide to be recorded simultaneously with limiting resolutions of 0.1, 0.2, and 0.4 nm (at  $50 \mu\text{m}$  entrance slit width) for the three gratings in the above order. In this work, we used the  $1200 \text{ nm}^{-1}$  grating, having a blaze wavelength of 500 nm, with a  $100 \mu\text{m}$  slit width. The wider slit results in a slightly lower resolution ( $\approx 0.3$  nm FWHM, or about 6 pixels), but was preferred for intensity reasons. The wavelength calibration of the chip was done for different settings of the grating according to the manufacturer's prescription, using a Hg lamp as a standard. We estimate the uncertainty in the measured band positions to be 0.1 nm or about  $5 \text{ cm}^{-1}$ . The spectral response of this system was calibrated in the range 350–1100 nm by means of a standard tungsten ribbon lamp.

It is worth emphasizing that the UV emission reported here is very weak, on the order of 100 times weaker than the "standard" visible  $N_2(B \rightarrow A)$  beam afterglow observed earlier by us.<sup>15</sup> High-resolution measurements such as the present one are therefore only possible employing optical

multichannel detection. Nevertheless, our very first observations of the UV afterglow were made using a miniature scanning spectrometer (Photon Technology International Inc., model "The Small One"). Complete with a thermoelectrically cooled photomultiplier tube, it was placed inside the vacuum close to the beam. Slow scans with photon counting detection yielded acceptable, but low-resolution ( $\approx 1$  nm) spectra of the same origin as those discussed below.

### III. RESULTS AND DISCUSSION

Figure 1 shows a typical spectrum of the beam afterglow measured in the near UV and visible ranges. In the red part of the spectrum the strong bands of the first positive (" $1^+$ ") system ( $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ ) dominate. They originate from the radiative cascade  $W \rightarrow B \rightarrow A$  studied in Ref. 15. Some bands on the extreme short-wavelength side of the spectrum are due to the  $N_2$  second positive (" $2^+$ ") transition ( $C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''$ ). Since the  $C$  state is very short lived [ $\tau_{\text{rad}} \approx 40$  ns (Ref. 1)], it is probably populated in the beam via a radiative cascade from some unidentified higher state. In the similar beam afterglow observations by Freund,<sup>19</sup> the radiative cascade from the  $E^3\Sigma_g^+$  state was held responsible for the  $2^+$  emission (see also Ref. 15). This cannot apply in the present work, however, since the associated  $E^3\Sigma_g^+ \rightarrow A^3\Sigma_u^+$  transitions<sup>19</sup> in the range 230–280 nm were not observed (with the glass filter removed). All other major features of the spectrum shown in Fig. 1 belong to a hitherto unknown band system. It appears in the form of progressions as marked in the 350–570 nm range and is ascribed in this work to the

$N_2(G \rightarrow W)$  transition. These bands are red degraded and have a width of about 1 nm. Two weak blue-degraded bands at 474.8 nm and 521.2 nm remain unidentified.

The identification and vibrational assignment of the  $G \rightarrow W$  progressions are based on the known vibrational constants of the combining states.<sup>8,20</sup> In the 400–550 nm region, two progressions are very obvious and were used for the initial analysis. Of a third progression, between  $\approx 380$  and 450 nm, some bands are somewhat overlapped. This progression served to confirm the results [see below, (Table I and Fig. 3)]. From the relative shift between the other two  $v''$  progressions  $\nu(v' + 1 \rightarrow v'') - \nu(v' \rightarrow v'')$ , a vibrational spacing in the upper state  $\Delta G'_{v+1/2} = 743 \pm 3 \text{ cm}^{-1}$  was observed. It is in perfect agreement with the accurately known spacing between the two lowest vibrational levels of the  $N_2(G^3\Delta_g)$  state  $\Delta G'_{1/2} = 742.49 \text{ cm}^{-1}$ .<sup>8,9</sup> Thus we ascribe the newly observed band system to emission from  $N_2(G)$  in its lowest vibrational levels. This latter conclusion is very reasonable, being in accord with the monotonically decreasing vibrational population which we have observed in other components of our  $N_2$  beam [ $N_2(W)$  (Ref. 15) and  $N_2(A)$  (Ref. 14)].

Having thus identified the upper state, almost the only possible candidate for the lower state had to be  $N_2(W^3\Delta_g)$  because of the wavelength range of the band system and the expected overall manifold of triplet states.<sup>10</sup> For a confirmation, the spacings between the members of the observed  $v''$  progressions were analyzed to give  $\Delta G''_{v+1/2}$  values, and these were matched with the known vibrational spacings of the  $N_2(W^3\Delta_g)$  state. Again the measured differences were found to agree within  $\pm 3 \text{ cm}^{-1}$  with those calculated from accurate  $W$ -state vibrational constants.<sup>20</sup> Owing to the anharmonicity of the  $W$  state, an unambiguous labeling of the vibrational levels was possible. For example, a particular vibrational spacing  $\Delta G''$  was measured as 1310 and 1309  $\text{cm}^{-1}$  from the  $(v' = 0, v'')$  and the  $(v' = 1, v'')$  progressions, respectively (cf. the four rightmost bands in Fig. 1). The average of 1309.5  $\text{cm}^{-1}$  compared very well with the calculated spacing  $\Delta G''_{7+1/2}$  in the  $W$  state (1310.92  $\text{cm}^{-1}$ ). By comparison,  $\Delta G''_{8+1/2} = 1287.01 \text{ cm}^{-1}$  and  $\Delta G''_{6+1/2} = 1334.91 \text{ cm}^{-1}$ , both of which can clearly be ruled out. The prominence of transitions into lower state levels with rather high vibrational quantum number is again as expected, considering the known radial displacement of the  $G$  and  $W$  states ( $r'_e = 1.61 \text{ \AA}$  (Ref. 8) and  $r''_e = 1.28 \text{ \AA}$  (Ref. 20)]. The red degradation of the bands is also consistent with the identification.

From these results, the origin of the  $N_2(G^3\Delta_g \rightarrow W^3\Delta_u)$  band system is obtained to lie at  $\nu_{00} = 29\,329 \pm 10 \text{ cm}^{-1}$ . With the known value of  $T_e(W) = 59\,805.8 \text{ cm}^{-1}$ , we find  $T_e(G) = 89\,505 \pm 10 \text{ cm}^{-1}$ . The latter value corresponds to 11.097 eV, in very good agreement with the predicted location of this state according to Refs. 8 and 10–12. In fact, the deviation from the experimental estimate of 10.8 eV given in Ref. 8 is in the expected direction. The extrapolation used in that work would tend to overestimate the dissociation energy of the  $G$  state and therefore place its potential minimum a little lower. The

TABLE I. Band positions and relative intensities of the  $N_2(G \rightarrow W)$  system.

Band	Band positions (nm, vac)		Relative intensities	
	Measured	Calculated <sup>a</sup>	Measured <sup>b</sup>	Calculated <sup>c</sup>
0-4 <sup>d</sup>	424.58	424.61	0.20	0.19
0-5	451.14	451.10	0.40	0.42
0-6	480.61	480.56	0.61	0.73
0-7	513.53	513.50	1.0	1.0
0-8 <sup>d</sup>	550.58	550.57	1.0	1.1
0-9 <sup>d</sup>	592.05	592.56	1.1	1.0
0-10 <sup>d</sup>	640.35	640.51	0.78	0.74
1-2	368.49	368.55	0.07	.05
1-3 <sup>d</sup>	389.08	389.09	0.26	.18
1-4	411.62	411.63	0.37	0.42
1-5	436.51	436.49	0.69	0.68
1-6	464.0	464.01	0.76	0.77
1-7	494.65	494.65	0.59	0.59
1-8	528.91	528.95	0.30	0.26
1-9		567.6	<0.05	0.03
2-3 <sup>d</sup>	378.65	378.51	0.18	0.24
2-4	399.81	399.81	0.41	0.41
2-5 <sup>d</sup>	423.25	423.21	0.43	0.44
2-6	448.99	449.04	0.31	0.27

<sup>a</sup>From  $\nu_{00} = 29\,329 \pm 10 \text{ cm}^{-1}$  as measured in this work and using the vibrational constants of the  $G$  and  $W$  states from Refs. 8 and 20, respectively.

<sup>b</sup>Areas under the bands, corrected for the relative spectral sensitivity of the detection system.

<sup>c</sup>Calculated as  $\nu^2 \cdot \text{FCF}(v'v'')$  and normalized separately in each progression to the band indicated (underlined).

<sup>d</sup>Bands are overlapped.

error limits of our results allow for the fact that no extrapolation to the true band origins was attempted. Instead, the band frequencies were simply obtained from the wavelengths at the peaks of the rotationally unresolved bands. However, the bands are very sharp. The fine structure splitting of both states is very small [ $A_G = -0.19 \text{ cm}^{-1}$  (Ref. 8) and  $A_W = 5.82 \text{ cm}^{-1}$  (Ref. 20)], and the rotational distribution of the emitting molecules is expected to be thermal with  $T_{\text{rot}} \approx 150 \text{ K}$  [according to detailed measurements on other long-lived species in the  $N_2$  beam  $N_2(A)$  (Ref. 16) and  $N_2(W)$  (Ref. 15)]. A comparison of the measured and calculated band positions is presented in Table I. The agreement is excellent throughout. Figure 2 shows the  $N_2(G)$  and  $N_2(W)$  state potential energy curves with their correct relative separation as determined in this work.

The assignment of the newly discovered transition is further supported by a consideration of the relative band intensities. Franck-Condon factors (FCFs) for the  $G, v' \rightarrow W, v''$  system were calculated from the known molecular constants.<sup>8,20</sup> They are presented in Table II. A comparison of the measured band intensities with those calculated in the FCF approximation is shown in Table I. The very good agreement is further proof of the correct identification of the new band system. Figure 3 gives a graphical representation of the calculated distribution of the transition probabilities in this system up to large wavelengths

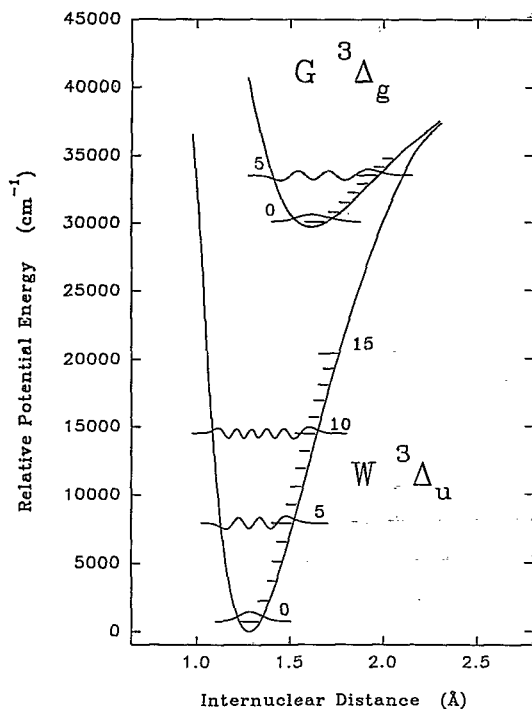


FIG. 2. Rydberg-Klein-Rees (RKR) potential energy curves calculated from molecular constants given in Refs. 8 and 20. The energy scale refers to the minimum of the  $W$ -state curve,  $v_{00}(G^3\Delta_g)$  and hence the relative spacing of the curves was obtained in this work.

( $v''=15$ ). In the upper state, only the vibrational levels  $v'=0-2$  have been included, with a relative weighting so as to match the observed relative intensities at the appropriate wavelengths. The figure shows the general structure of this new band system in a wide spectral range, but is not intended as a simulation of the experimental spectrum, (Fig. 1). The latter depends not only on the apparatus response function, but also on the varying width of the bands. Table I provides the direct comparison of the true measured and the calculated intensities.

Only the transitions from  $G$ ,  $v'=0-2$  were unambiguously identified in the spectrum. Transitions from  $v'=3$  are overlapped in the region  $\lambda < 380$  nm with  $v'=1$  bands (see Table II) and cannot be clearly separated. Some bands in the UV part of the spectrum can be tentatively assigned to higher  $v'$  bands (7-2)–321.7 nm; (5-2)–334.9 nm; (4-2)–342.3 nm; (5-3)–351.8 nm; (4-3)–359.8 nm. However this identification is not safe since the corresponding progressions are not well developed.

The radiative lifetime of the  $G$  state was estimated from the decrease of the emission intensity as recorded at two distances from the discharge  $s=25$  and  $55$  cm. This difference corresponds to a time of flight of the  $N_2^*$  molecules of about  $310 \mu s$ .<sup>14</sup> The intensity decrease of the  $G$ ,  $0 \rightarrow W$ , 7 band at  $513$  nm was then normalized against that of the  $1+$  band  $B$ ,  $3 \rightarrow A$ , 0 band at  $686$  nm. The apparent lifetime of the latter band was measured in Ref. 15 to be  $165 \mu s$ . This method gives for the lifetime of the  $G$  state an estimate of  $\tau_r(G) \geq 200 \mu s$ . The spectra taken at the two distances were very similar, indicating that the lifetime is independent of the vibrational level in the range  $G$ ,  $v'=0-$

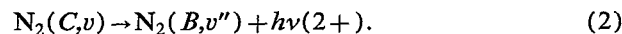
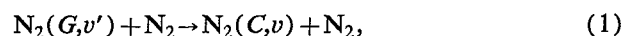
2. Unlike Ref. 15, a direct lifetime measurement from the intensity falloff with increasing distance is here not possible because of the light collection optics and scattering cell used in the present work; the divergence of the beam then introduces geometry factors for the detection efficiency which are not reliably known (see Ref. 17).

Note that in principle the observed apparent lifetime could be that of some higher state feeding the  $G$  state radiatively, which itself could be short lived (analogous to the situation with the  $B \rightarrow A$  beam afterglow<sup>15</sup>). However, it would then be difficult to understand why  $G \rightarrow W$  emission has never been observed in discharges, where surely the  $G$  state will also be populated directly by electron impact. Thus we believe that the measured lifetime is actually that of the  $G$  state itself.

It is definitely this long radiative lifetime which has also prevented the observation of  $G$  state in flow systems. In any collisional environment, quenching of the  $G$  state will largely suppress its emission. Unfortunately, this also thwarts attempts to use the standard LIF technique on the  $G \leftarrow W$  transition, such as has been proposed as a way to monitor the  $W$  state population.<sup>13</sup> This quantity is important in the collision dynamics of the  $N_2$  triplet manifold.<sup>13,17,18,21-23</sup> However, there may be a variant of the LIF method which circumvents this problem. Noting that the  $N_2(C^3\Pi_u)$  state is almost isoenergetic with the  $G$  state, collision-induced intramolecular transitions  $G^3\Delta_g \rightarrow C^3\Pi_u$  may be facile [see our related work on  $A \rightarrow B$  and  $W \rightarrow B$  transfer (Ref. 17 and 18)]. The “2+” emission from the (short-lived)  $C$  state could be used as a “secondary” LIF signal subsequent to  $G \leftarrow W$  laser excitation and  $G \rightarrow C$  collisional transfer. This could then be a diagnostic tool to monitor the  $W$  state.

On the other hand, the Franck-Condon factors between the  $G$  and  $C$  states are expected to be very small for low vibrational levels. A preliminary experimental test was therefore undertaken to indicate if, basically, the possibility of such an energy transfer exists. To this end, the collision cell was filled with 4 mbar of  $N_2$  (with  $N_2$  target gas, both intra- and intermolecular transfer can be effective). The intensity of the  $C$ ,  $0 \rightarrow B$ ,  $v''$  “2+” bands did, in fact, increase by a factor of 2, and the  $C$ ,  $1 \rightarrow B$ ,  $v''$  progression appeared. By contrast, the  $G \rightarrow W$  bands were decreased by a factor of 2, about the amount expected to result from elastic plus energy transfer scattering.<sup>17</sup>

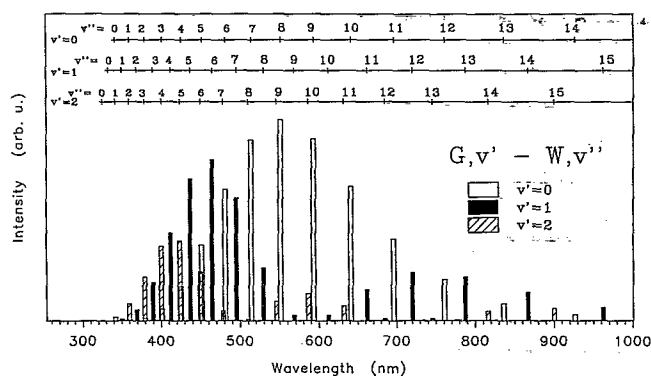
The collision-induced increase of the 2+ emission, pending the unequivocal identification of the reactant state, can be taken tentatively as evidence of the proposed reaction sequence



The rate constant for reaction (1)  $k_1(N_2)$  can roughly be estimated from the intensity ratio of the total emission in the 2+ bands  $I_C$  and in the  $G \leftarrow W$  bands  $I_G$  with the collision cell filled

TABLE II. Franck-Condon factors<sup>a</sup> and band positions (nm) for the  $G^3\Delta_g, v' - W^3\Delta_u, v''$  transition in  $N_2$ .

$v'' \backslash v'$	0	1	2	3	4	5	6
0	0.504E-5 341.0	0.408E-4 332.5	0.176E-3 324.8	0.542E-3 317.6	0.133E-2 311.0	0.277E-2 304.9	0.508E-2 299.2
1	0.834E-4 359.1	0.569E-3 349.8	0.207E-2 341.2	0.533E-2 333.3	0.109E-1 326.0	0.187E-1 319.3	0.282E-1 313.0
2	0.660E-3 378.9	0.372E-2 368.6	0.111E-1 359.0	0.231E-1 350.3	0.378E-1 342.3	0.512E-1 334.8	0.594E-1 328.0
3	0.332E-2 400.7	0.149E-1 389.1	0.350E-1 378.5	0.562E-1 368.8	0.684E-1 359.9	0.659E-1 351.7	0.503E-1 344.2
4	0.118E-1 424.6	0.408E-1 411.6	0.706E-1 399.8	0.792E-1 389.0	0.614E-1 379.1	0.309E-1 370.0	0.704E-2 361.7
5	0.318E-1 451.1	0.786E-1 436.5	0.903E-1 423.2	0.573E-1 411.1	0.160E-1 400.1	0.423E-6 390.0	0.110E-1 380.7
6	0.667E-1 480.6	0.107E+0 464.0	0.653E-1 449.0	0.102E-1 435.5	0.347E-2 423.1	0.283E-1 411.8	0.416E-1 401.5
7	0.112E+0 513.5	0.990E-1 494.6	0.156E-1 477.7	0.696E-2 462.3	0.419E-1 448.4	0.441E-1 435.8	0.166E-1 424.2
8	0.153E+0 550.6	0.522E-1 528.9	0.297E-2 509.6	0.498E-1 492.2	0.458E-1 476.4	0.764E-2 462.2	0.366E-2 449.2
9	0.173E+0 592.5	0.665E-2 567.6	0.454E-1 545.3	0.569E-1 525.4	0.562E-2 507.5	0.114E-1 491.4	0.376E-1 476.8
10	0.161E+0 640.5	0.833E-2 611.4	0.799E-1 585.7	0.134E-1 562.8	0.144E-1 542.3	0.459E-1 523.9	0.210E-1 507.3
11	0.126E+0 695.7	0.604E-1 661.6	0.538E-1 631.5	0.609E-2 605.0	0.542E-1 581.4	0.203E-1 560.3	0.194E-2 541.4
12	0.824E-1 760.0	0.120E+0 719.4	0.665E-2 684.0	0.545E-1 653.0	0.331E-1 625.6	0.269E-2 601.2	0.381E-1 579.5
13	0.452E-1 835.7	0.142E+0 786.9	0.116E-1 744.8	0.701E-1 708.1	0.344E-6 676.0	0.439E-1 647.7	0.268E-1 622.5
14	0.209E-1 926.1	0.121E+0 866.5	0.723E-1 815.7	0.247E-1 772.0	0.358E-1 734.0	0.404E-1 700.7	0.574E-3 671.3
15	0.811E-2 1035.8	0.789E-1 961.9	0.127E+0 899.7	0.111E-2 846.8	0.703E-1 801.2	0.103E-2 761.7	0.391E-1 727.2
16	0.264E-2 1171.8	0.406E-1 1078.1	0.132E+0 1000.6	0.489E-1 935.5	0.337E-1 880.3	0.291E-1 832.8	0.407E-1 791.7
17	0.721E-3 1344.6	0.168E-1 1222.6	0.953E-1 1123.9	0.115E+0 1042.5	0.338E-4 974.3	0.686E-1 916.5	0.969E-3 866.9

<sup>a</sup>For example, 0.1E-1 means  $0.1 \times 10^{-1}$ .FIG. 3. A bar diagram of the relative transition probabilities of the  $N_2(G \rightarrow W)$  band system, calculated as  $v' \cdot \text{FCF}$  and normalized as in Table I. Three  $v''$  progressions are shown for  $v' = 0, 1$ , and  $2$  as marked.

$$\frac{I_C}{I_G} = \frac{k_1(N_2) \cdot (N_2)}{1/\tau_r(G)} \quad (3)$$

Here the second ( $N_2$ ) is the density of the target  $N_2$  gas in the cell.  $I_C/I_G$  was found to be  $\approx 1$ . Using the result  $\tau_r(G) \geq 200 \mu\text{s}$  from above gives an estimate of  $k_1(N_2) \leq 5 \times 10^{-11} \text{ cm}^3/\text{s}$ . Rate constants of this magnitude would certainly make reactions (1) and (2) a viable method of monitoring the  $W$  state through  $G \leftarrow W$  excitation at total pressures on the order of 1 Torr.

In conclusion, we can state that this experiment has again demonstrated the usefulness of the spontaneous as well as the collision-induced beam afterglow as a technique to study the delicate, high-lying states of  $N_2$  (and certainly of many other molecules, too). At the relatively high pressure of most standard spectroscopic sources, such states are easily quenched by collisions.

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