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Radiative Lifetime Measuements of Some Excited States of N_2^+ and CH

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Time-sampling technique has been applied to radiative lifetime measurements. The time resolution of the apparatus was about 10 nsec. The excited molecules were produced by electron bombardment of N_2 and CH_4. The measured lifetimes of $N_2^+(B^2\sum_u^+)$, $CH(A^2\Delta)$ and $CH(B^2\sum^-)$ are $(6.5\pm0.5)\times10^{-8}$ sec, $(4.3\pm0.2)\times10^{-7}$ sec and $(7.6\pm0.4)\times10^{-7}$ sec, respectively. Band oscillator strengths have been computed on the assumption that the electronic transition moment is constant in the range in which the transition takes place.

For the study of unstable chemical species such as ions and free radicals, the knowledge of radiative lifetime is indispensable. As a matter of principle transition probabilities and oscillater strengths can be determined by measuring absorption coefficients. Some investigations[1,2] on OH and CN molecules along this line have been reported. However, there are difficulties in the determination of absorption coefficients of unstable chemical species. Experimental data on the measurements of the concentration of the molecules excited to upper states are not always available.

On the other hand, it is possible to calculate reliable transition probabilities and oscillator strengths from the measurements of the radiative lifetime. The lifetime measurements for a number of well known molecule transitions have recently been reported. The following two methods have been reported on the measurements of the lifetime.

(a) Direct measurement of decay time[3,4]
(b) Phase shift method[5,6]

The radiative lifetimes fall in the range 10^{-9} to 10^{-6} sec for allowed transitions. In (a), the lifetime is obtained from the decay time of the emitted light. Thus a good time resolution is required in the apparatus.

In this paper, the results of the lifetime measurements of $N_2^+(B^2\sum_u^+)$, $CH(A^2\Delta)$ and $CH(B^2\sum^-)$ by means of the time sampling method are reported. These excited molecules are produced by pulsed beam electron impact below 300 eV.

Absorption oscillator strengths of the $N_2^+(B^2\sum_u^+ X^2\sum_g^+)$, the $CH(A^2\Delta-X^2\Pi)$ and the CH $(B^2\sum^- -X^2\Pi)$ are calculated on the assumption that the

1) O. Oldenberg and F. F. Rieke, *J. Chem. Phys.*, **6**, 439, 779 (1938).
2) P. J. Dyne, *ibid.*, **28**, 999 (1958).
3) R. G. Bennet and F. W. Dalby, *ibid.*, **31**, 434 (1959).
4) M. Jeunehomme, *ibid.*, **44**, 2672 (1966).
5) E. H. Fink and K. H. Welge, *Z. Naturforsch.*, **19a**, 1193 (1964).
6) G. M. Lawrence, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 359 (1965).

electronic transition moment is constant in the range in which the transition takes place.

Theory

The radiative lifetime $\tau_{v'}$ of the upper vibrational level in an electronic transition can be expressed by summing over fine structures due to rotational and electron spin

$$1/\tau_{v'} = A_{v'} = \sum_{v''} A_{v'v''} \tag{1}$$

where $A_{v'v''}$ is the Einstein coefficient. The oscillator strength $f_{v'v''}$ is defined as

$$f_{v'v''} = 1.51 \cdot (G'/G'') \cdot A_{v'v''} \cdot \lambda^2_{v'v''} \tag{2}$$

where λ is the wavelength in cm, $A_{v'v''}$ in $\sec^{-1}$ and G'/G'' is equal to the ratio of the upper to lower electronic statistical weights as defined by Mulliken.[7]

The band intensity is related to the Franck-Condon factor $q_{v'v''}$[8] as

$$I_{v'v''} = K \cdot N_{v'} \cdot \lambda^{-4}{}_{v'v''} \cdot R_e^2 \cdot q_{v'v''} \tag{3}$$

where K is a constant, $N_{v'}$ is the population of the upper vibrational level v'. R_e is an electronic transition moment. On the assumption that R_e is not a slowly varying function of the internuclear distance but a constant for all v'-v'' transitions in a given band system, the ratio $A_{v'v''}/A_{v'}$ is expressed as

$$A_{v'v''}/A_{v'} = q_{v'v''} \cdot \lambda^{-3}{}_{v'v''} / \sum_{v''} q_{v'v''} \cdot \lambda^{-3}{}_{v'v''} \tag{4}$$

$A_{v'v''}$ can be expressed by the product of $A_{v'}$ and the Franck-Condon factor to a good approximation.

$$A_{v'v''} = A_{v'} \cdot q_{v'v''} \tag{5}$$

In order to calculate the oscillator strengths for individual bands, the theoretical computations of the Franck-Condon factors must be available.

Experimental

An electron gun was used for the formation and excitation of unstable molecules from sample gases. Figure 1 shows a schematic diagram of the electron gun. The emitter is an indirectly-heated oxide-coated cathode which emits at a temperature below 1000°K. However, it can be poisoned easily by organic or other vapors with loss of emission and discoloration. The electron energy can be varied from 30 to 300 eV, and a current about 3 mA can be produced. The first grid is a control grid which is biased by a potential of -50 V.

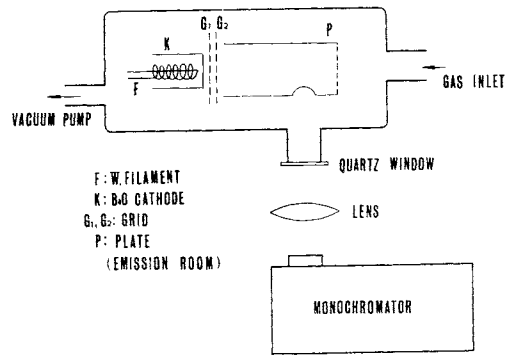

Fig. 1. Schematic diagram of the electron gun.

The pulse applied to the control grid is 50 V in amplitude and is controllable in duration up to 1.0 μsec. The rise and fall time of this pulse is 4.0×10^{-9} sec (4 nsec) and 6.0×10^{-9} sec (6 nsec), respectively. The excitation room is a cylindrical plate, 8 mm in diameter and 20 mm in length. The emitted light can be taken out from the hole, 6 mm in diameter, as shown in Fig. 1. The emitted light is made monochromatic with a small Nippon-Jarrel Ash grating monochromator.

A good time resolution is required for the measurements of lifetimes. In order to measure periodic faint

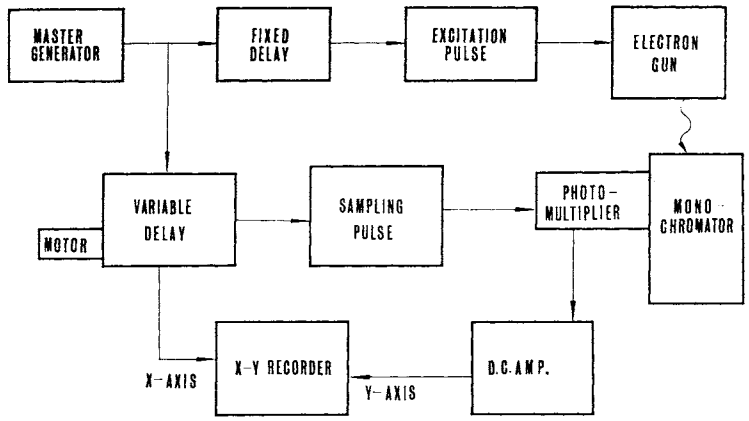

Fig. 2. Block diagram of the apparatus.

7) R. S. Mulliken, *J. Chem. Phys.*, **7**, 14 (1939).
8) G. Herzberg, "Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules," CD Van Nostland CO., Inc., Princeton, N. J. (1950)

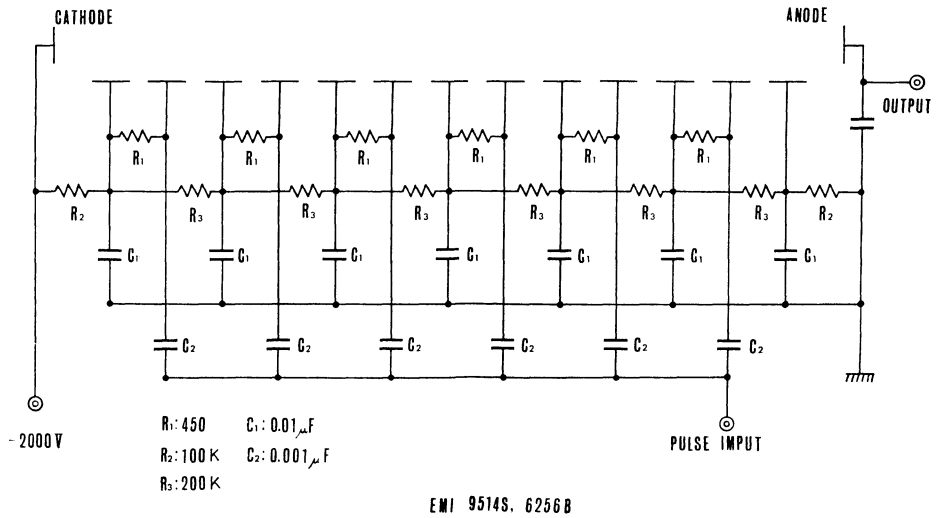

Fig. 3. Circuit of the pulsed photomultiplier.

light intensity, the photomultiplier sampling technique[9] can be utilized. Thus, the pulsed photomultiplier samples the output of periodically emitted light, and this sampling pulse is phased slowly by means of the variable delay circuit. The emitted light is then recorded as a function of time on a X-Y recorder. The advantage of this method is that the output current inside the phototube can be combined to the high-input impedance vacuum-tube voltmeter to detect very faint light. This sampling technique is applicable to time-resolved spectroscopy at a fixed phase of a periodic light. The block diagram of the apparatus is shown in Fig. 2. The master generator produces two equal pluses at a repetition rate variable from 1 to 10 k Hz. One pulse is fed to the Control grid of the electron gun after a fixed delay circuit, and the other initiates the sampling pulse. Th delay time of this pulse increases slowly and continuously by a motor-driven 50 kΩ variable resistance. The variable delay network consists of a phantastron circuit and a cathode follower. The delay time can be moved to 10 μsec in six steps. The pulse applied to photomultiplier is 100 V in amplitude. The 3C-2V coaxial cable is used as a pulse-forming network, and its length determines the pulse duration. The minimum pulse duration obtained is about 20 nsec. The sampled phototube signal is integrated with a simple RC network by which the time constant of the recording system is determined. The output of the voltmeter is recorded on the X-Y recorder, and the delay time is scanned at a rate determined by the speed of the motor and the grear ratio.

Figure 3 indicates a schematic diagram of the pulsed photomultiplier circuit. The method which has been most widely used is that in which the high voltage pulse is applied directly to the cathode and the dynodes.[9] However, it is difficult technically to produce an extremely stabilized high-voltage pulse, which is needed to reduce fluctuations of the phototube gain. The dynodecontrolled technique is therefore used in the present measurements.[10] The gating pulse is applied to the alternate dynodes throught the load resistance, the potentials of which are the same as those of the adjacent dynodes during the closed-gate period. EMI 9514S and 6256B as the head-on type photomultiplier and in some cases 931A and 1P21 as the side-window type are used for detection of light.

Since the actual gated period is equal to the sampling pulse duration minus the transit time of the electron in the photomultiplier, the time resolution is ultimately determined by the transit time spread.[11] In the dynode-controlled technique, the background current during the closed gate period must also be controlled to a lower value in order to obtain better time resolution.

Results and Discussion

Lifetime Measurements. a) *He Lines.* Measurements of the radiative lifetime of three excited states are summarized in Table 1. Our data agree well with those of other investigators within the range of experimental errors. Measurements were made at an electron energy of 80 eV.

Table 1. Lifetimes of He terms[a]

	4^3S-2^3P 3188 Å	3^3P-2^3S 3889 Å	3^1P-2^1S 5016 Å
Heron *et al.*[12]	6.75±0.1	11.5±0.5	7.4±0.1
Bennet and Dalby[3]	7.75±0.4	10.6±0.5	≦1.5
Lawrence[6]	—	10.5±0.5	—
This work	7.3±0.3	10.4±0.6	3.0±0.5[b]

a) Unit: 10^{-8} sec
b) This value was measured at a gas pressure of 11 μ.

9) C. F. Hendee and W. B. Brown, *Philips. Tech. Rev.*, **19**, 50 (1958).

10) H. M. Crosswhite, D. W. Steinhaus and G. H. Dieke, *J. Opt. Soc. Amer.*, **41**, 299 (1951).

11) S. Minami and K. Nishikawa, *Applied Opts.*, **5**, 173 (1968).

Variations of the lifetime with the gas pressure were examined. However, except for that of 3^1P level no significant dependence was recognized within the range of the gas pressure from 1.0 μ to 10 μ. It is well known that the 3^1P-2^1S transition is affected by the trapping of resonance radiation because of 3^1P level corresponding to the upper level of the 537A resonance line.[12] Our data for the 3^1P level

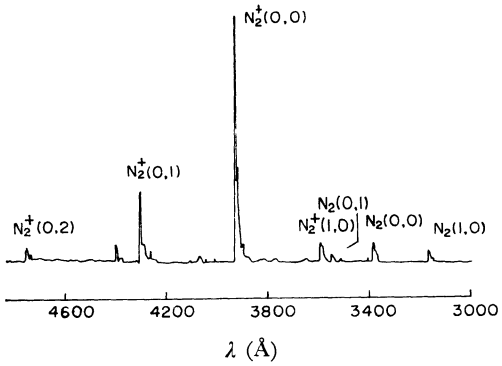

Fig. 4. Emission spectrum obtained from nitrogen (gas pressure 5 μ) excited by 120 eV electrons.

shown in Table 1 were obtained at a gas pressure of 11 μ. Because of the decrease of the trapped resonance radiation, the lifetime measured at a lower pressure can be considered to be a measure of the resolving time of the apparatus. The minimum resolving time obtained was about 10 nsec.

b) $B^2\Sigma_u^+$ *State of* N_2^+. Figure 4 shows the emission spectrum obtained from the bombardment of N_2 gas at an electron beam of 120 eV. The measurement was made at a pressure of 5 μ. The spectrum consists of the $B^2\Sigma_u^+$-$X^2\Sigma_g^+$ system of N_2^+ and the $C^3\Pi_u$-$B^3\Pi_g$ system of N_2. The result agrees well with those of other measurements.[3,5] The radiative lifetime was measured by use of 0.5 m grating monochromator (about 15Å bandwidth) in order to separate various emission bands. The dependence of the lifetime for the (0,0) band of N_2^+ upon the electron energy is shown in Fig. 5. The apparent lifetime increases slowly up to an electron energy of 100 eV, and remains constant beyond it. A similar tendency has been reported by Bennet and Dalby,[3] who assumed that this was due to a mixing of other bands, since they used interference filters of about 100Å bandwidth instead of a monochromator. The fact that our experiments with a monochromator showed a similar tendency indicates that their interpretation is not correct. This cannot be ascribed to the cascade population of the $N_2^+(B^2\Sigma_u^+)$, because no higher electronic states are known from which the transitions to this level are allowed. It is highly desirable to investigate the lifetime down to the excitation threshold.[13] However, the measurements near the threshold were unreliable because of the low signal level compared with the noise level. The value obtained above 100 eV was taken as the lifetime of the N_2^+ $(B^2\Sigma_u^+)$. A lifetime

$$(6.5\pm0.5)\times10^{-8}\ \text{sec}$$

was obtained. The variation of the lifetime with gas pressure was not recognized within the range of our experiments from 1 μ to 5 μ. It can be considered that neither the collision quenching effect nor the trapped resonance radiation has significant influence on the lifetime in the range of the gas pressure below 5 μ.[4] The decay curve

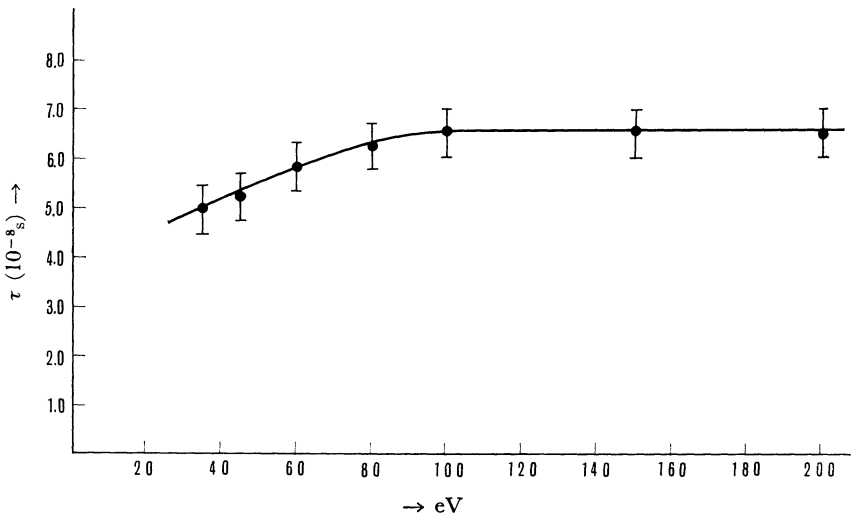

Fig. 5. The dependancy of the lifetime of the $N_2^+(B^2\Sigma_u^+)$ level upon electron energy.

12) S. Heron, R. W. P. Mcwhirter and E. H. Rhoderick, *Proc. Roy. Soc., Ser. A*, **234**, 565 (1956).

13) R. E. Fox, *J. Chem. Phys.*, **35**, 1379 (1961).

was plotted as a function of time on semilogarith mic graph paper to determine the mean lifetimes. The observed decay was closely exponential.

c) $A^2\Delta$ and $B^2\sum^-$ States of CH. Figure 6 shows the spectrum obtained when CH_4 was bombarded with 100 eV electrons. The spectrum was taken with a small grating monochromator (15 Å bandwidth). The emission bands of the CH($A^2\Delta$-$X^2\Pi$) and the CH($B^2\sum^-$-$X^2\Pi$) are observed together with several atomic lines such as H_β, H_γ and H_δ. There are some other emission bands which seem to be those of CO^+. The formation of CO^+ is perhaps due to the reactons between the excited carbons and the oxide coated cathode. Similar

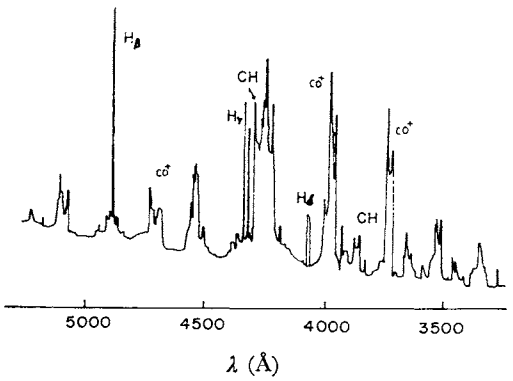

Fig. 6. Spectrum observed when methane (gas pressure of 5 μ) was bombarded with 100 eV electrons. The monochromator (15 Å bandwidth) was used.

results were also obtained from the bombardment of C_2H_4 and C_2H_6. The strong band observed at 4300 Å is the (0,0) band of the ($A^2\Delta$–$X^2\Pi$) system of CH. The (0,0) band of the ($B^2\sum^-$–$X^2\Pi$) system of CH is observed near 3900 Å though its intensity is small.[14,15] The radiative lifetimes were measured by use of a small monochromator in order to separate interfering bands. The dependence of the apparent lifetime of the CH($A^2\Delta$) state upon the electron energy is shown in Fig. 7. The lifetime is almost constant within the range of the electron energy from 40 eV to 150 eV. Below 40 eV, the emitted light intensity decreases so markedly that no accurate measurements can be done. The lifetime of the CH($A^2\Delta$) state was independent of the pressure in the range from 1 μ to 10 μ. Similar results have been reported.[16,17] It seems that both the collision quenching and the trapped resonance radiation do not occur. The duration of the pulsed electron beam was 1.0 μsec. The sampling pulse width was varied up to 0.3 μsec, but the change of lifetime was negligible. We conclude the lifetime for the CH($A^2\Delta$) level as

$$(4.3\pm0.2)\times10^{-7}\,\text{sec}$$

This value is a little lower than those of Bennet and Dalby,[16] and Fink and Welge.[17] Bennet and Dalby used interference filters with the 100 Å bandwidth for the lifetime measurements. Fink and Welge measured τ using the phase shift method with the 20 Å bandwidth monochromator. The bandwidth in our experiment was the same as that of Fink and Welge. The lifetime for the CH($B^2\sum^-$) level

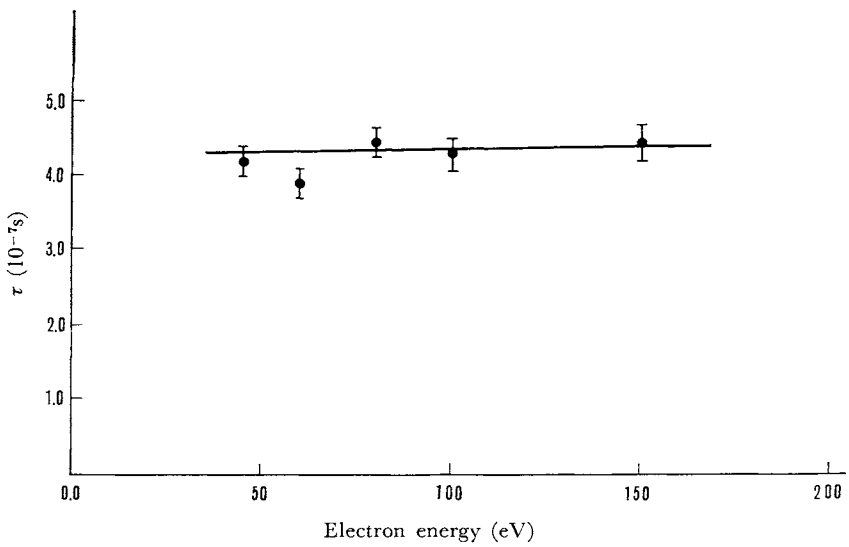

Fig. 7. The dependancy of the lifetime of the CH($A^2\Delta$) level upon electron energy.

14) L. Wallace, *Astrophys. J.*, **68**, 164 (1962).
15) R. W. B. Pearce and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman & Hall Ltd., London (1950).
16) R. G. Bernnet and F. W. Dalby, *J. Chem. Phys.*, **32**, 1716 (1960).
17) E. H. Fink and K. H. Welge, *ibid.*, **46**, 4315 (1967).

at an electron energy of 100 eV was

$$(7.6\pm0.4)\times10^{-7}\ \text{sec}$$

No variation of lifetime with the gas pressure was observed within the range from 5 μ to 10 μ. Precise investigations below 100 eV could not be done for the CH($B^2\sum^-$) state because the intensity of the emitted light was too small.

It should be examined whether cascading effects from higher electronic states occur. However, higher electronic states allowed to combine with $A^2\Delta$ and $B^2\sum^-$ are not yet known. Therefore, it may be assumed that the possibility of cascading effects is ruled out.

Oscillator Strength. Oscillator strengths $f_{v'v''}$ for individual bands can be calculated from Eq. (2), using the lifetimes of the upper level v'. It is necessary to know the theoretical calculations of the Frannck-Condon factors $q_{v'v''}$. Nicholls[18] has computed them numerically for the various band systems of N_2 and N_2^+. The oscillator strengths for the (0,0) band of the ($B^2\sum_u^+$–$X^2\sum_g^+$) of N_2^+ is evaluated using q_{00} value of Nicholls to be

$$f_{00}=(2.3\pm0.2)\times10^{-2},$$

where the wavelength used is 3914 A. G'/G'' is equal to unity. This value agrees very well with the results of Jeunehomme, $(2.47\pm0.18)\times10^{-2}$. Similar calculations were made for the (0.0) bands of CH($A^2\Delta$–$X^2\Pi$) and CH($B^2\sum^-$–$X^2\Pi$) respectively. Recently, Huo[19] has computed the Franck-Condon factor q_{00} for the ($A^2\Delta$–$X^2\Pi$) transition of CH. By use of Huo's value ($q_{00}=0.9905$), for the (0,0) band of CH($A^2\Delta$–$X^2\Pi$),

$$f_{00}=(6.5\pm0.3)\times10^{-3}$$

was obtained. The wavelength used is 4313 Å. For the CH($B^2\sum^-$—$X^2\Pi$),

$$f_{00}/q_{00}=(1.5\pm0.1)\times10^{-3}$$

was obtained. No theoretical calculation of the Franck-Condon factor for the above electronic transition has been reported. Hence, f_{00}/q_{00} was calculated insted of f_{00}. The wavelength used is 3880 Å. The results of this work are summarized in Table 2.

TABLE 2.

Molecule	Transition	Lifetime (10^{-8} sec)	Oscillator strength
N_2^+	$B^2\sum_u^+$–$X^2\sum_g^+$	6.5±0.5	0.023±0.002[a]
CH	$A^2\Delta$–$X^2\Pi$	43±2.0	0.0065±0.0003
CH	$B^2\sum^-$–$X^2\Pi$	76±4.0	0.0015±0.0001[b]

a) The calculated Franck-Condon factor is that of Nicholls.[18]
b) This value is f_{00}/q_{00} instead of f_{00}.

In the calculation of the oscillator strengths, as described previously, we assumed that electronic transition moment is independent of the internuclear separations.

The authors are indebted to Mr. Hiroshi Yamamoto of Toshiba Co., Ltd., for his assistance in designing and constructing the electron gun.

18) R. W. Nicholls, *J. Res. Nat. Bur. Stand. A*, **65**, 451 (1961).

19) W. M. Huo, *J. Chem. Phys.*, **49**, 1482 (1968).