

CHEMILUMINESCENT REACTIONS OF OZONE WITH 2,5-DIMETHYLFURAN, FURFURAL AND PYRROLE

PAWAN K. ARORA[†]

Air Monitoring Section, Bhabha Atomic Research Centre, Bombay 400085 (India)

(Received October 10, 1985; in revised form April 10, 1986)

Summary

Chemiluminescent reactions of ozone with 2,5-dimethylfuran, furfural and pyrrole have been studied in the gas phase at low pressures. The emitting species have been identified as HCHO(¹A₂), glyoxal(³A_u) and OH(X, $\nu = 4 - 9$) Meinel bands in the reaction of 2,5-dimethylfuran and α -dicarbonyl compound in the case of furfural. The reaction of pyrrole gives emission due to CHO(C), CH(² Δ), glyoxal(³A_u) and OH(X, $\nu = 4 - 9$) Meinel bands. Reaction pathways for the formation of excited molecules are proposed. Evidence is given that excited formaldehyde may be formed from the decomposition of a dioxetane.

1. Introduction

In the previous papers in this series we reported the results of gas phase chemiluminescent reactions of ozone with ring compounds such as monoterpenes [1, 2], thiophene [3] and furan [4]. The emitting species were identified and possible reaction mechanisms were proposed. In this paper we report similar studies for the reactions of ozone with 2,5-dimethylfuran, furfural and pyrrole. Kummer *et al.* [5] were the first to observe chemiluminescence from the reaction of ozone with 2,5-dimethylfuran but no spectrum was reported. In this work, we have observed formaldehyde fluorescence, glyoxal phosphorescence and Meinel bands emission in the reaction of ozone with 2,5-dimethylfuran while the furfural reaction gave rise to emission from an α -dicarbonyl compound. The chemiluminescence spectra from the reaction of ozone with pyrrole showed major emission features due to CHO, CH(² Δ), glyoxal(³A_u) and Meinel bands. Reaction pathways for the formation of excited molecules are proposed. Evidence is given to show that excited formaldehyde may be formed from the decomposition of a dioxetane.

[†]Present address: Research and Development Centre, Universal Ferro and Allied Chemicals Ltd., S. V. Road, Manpada, Thane 400607, India.

2. Experimental details

The experimental system has been described in detail elsewhere [1]. It mainly consists of a quartz reaction cell coupled to a 0.25 m monochromator (Jarrel-Ash). Ozone from a Welsbach-type ozone generator [6] was mixed with the reactant at low pressure and the light emission was detected with either an EMI 9635QA photomultiplier tube (for the UV and the visible region) or a thermoelectrically cooled EMI 9659A photomultiplier tube (for the region up to 900 nm). A dual-channel photon counter was used for processing the signal. The monochromator-photomultiplier tube combination was calibrated for its efficiency by using a standard tungsten lamp whose colour temperature was 3015 K.

2,5-Dimethylfuran (Fluka AG) from a fresh bottle was used as received while pyrrole and furfural were distilled before use. Helium (grade 4.5) was used as the carrier gas. The pressure in the reaction cell was measured with an MKS Baratron pressure sensor (type 310 BHS-1000).

3. Results

All spectra were corrected for the efficiency of the monochromator and photomultiplier tube. This was carried out on a Norsk Data 560/X computer network. The uncorrected spectra were read on a Tektronix Graphic Tablet facility. The data points were corrected for the efficiency of

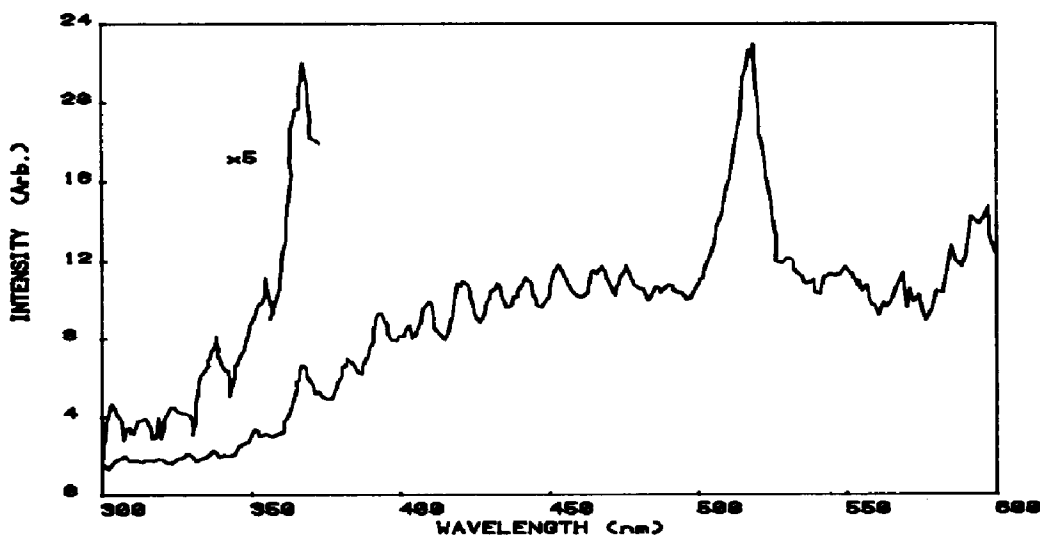


Fig. 1. Chemiluminescence spectrum from the reaction of ozone with 2,5-dimethylfuran (spectral slitwidth, 3.3 nm; total pressure, 19.5 Torr; ozone, 0.2 Torr; 2,5-dimethylfuran, 0.54 Torr).

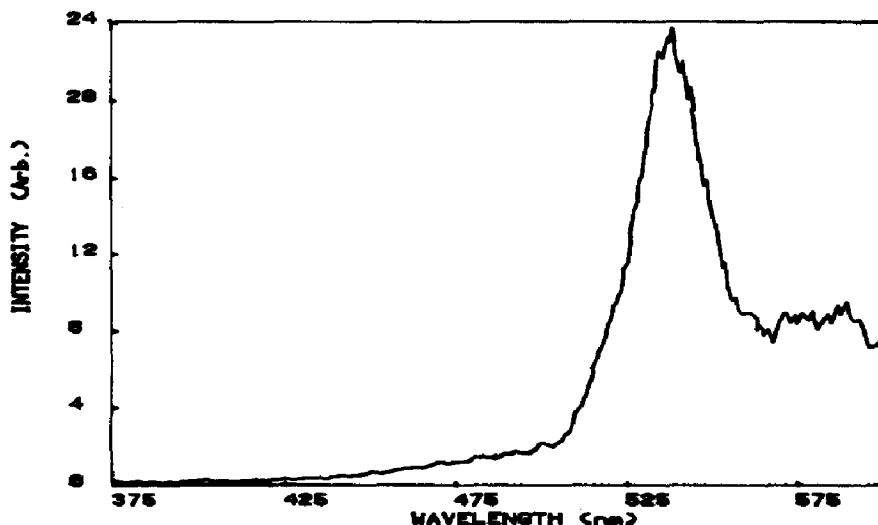


Fig. 2. Chemiluminescence spectrum from the reaction of ozone with furfural (spectral slitwidth, 10 nm; total pressure, 330 Torr; ozone, 1 Torr; furfural, 0.46 Torr).

the system by using the calibration factors obtained earlier. These were then plotted on a Tektronix interactive digital plotter by using Plot-10 software.

Figure 1 shows the chemiluminescence spectrum from the reaction of ozone with 2,5-dimethylfuran. The emission starts from 335 nm and extends up to 600 nm. The peaks in the emission spectrum up to 500 nm are attributed to different transitions from the 4^1 and 4^0 vibrational levels of the excited state 1A_2 to the ground state 1A_1 of H_2CO . However, the vibronic hot band centred at 342 nm is due to the transitions originating from the 4^3 and the 2^14^1 levels. The intensity of the emission was not sufficient to resolve these transitions, which occurred at 343 nm and 339 nm respectively. The spectra were recorded at three different total pressures, *i.e.* 2.86, 9.7 and 19.5 Torr, by throttling the pumping speed. It was observed that the peak-to-valley ratio for all the peaks increased with total pressure and its values for the 422 nm peak were 1.19, 1.32 and 1.38 respectively. The peak at 520 nm is the well-known 0_0^0 band of the $^3A_u \rightarrow ^1A_g$ transition of glyoxal.

Figure 2 shows the chemiluminescence spectrum from the reaction of ozone with furfural. The spectrum was studied from 300 to 900 nm and only emission in the region 400 - 600 nm with a broad peak at 535 nm was observed. A weak shoulder to the main peak was also recorded at 575 nm. The half-bandwidth of the main peak was about 27 nm. This indicates that the emission is probably due to an α -dicarbonyl compound. The spectrum could be observed only at a total pressure of 330 Torr.

The chemiluminescence spectrum from the reaction of ozone with pyrrole at a total pressure of 2.2 Torr is shown in Fig. 3. The emission starts from 300 nm and shows major features due to CHO, $CH(^2\Delta \rightarrow ^2\Pi)$, glyoxal- (3A_u) and $OH(^2\Pi, \nu < 9)$. The spectrum was taken with only 9 mTorr pyrrole because if more pyrrole was introduced a yellow coating on the reaction cell

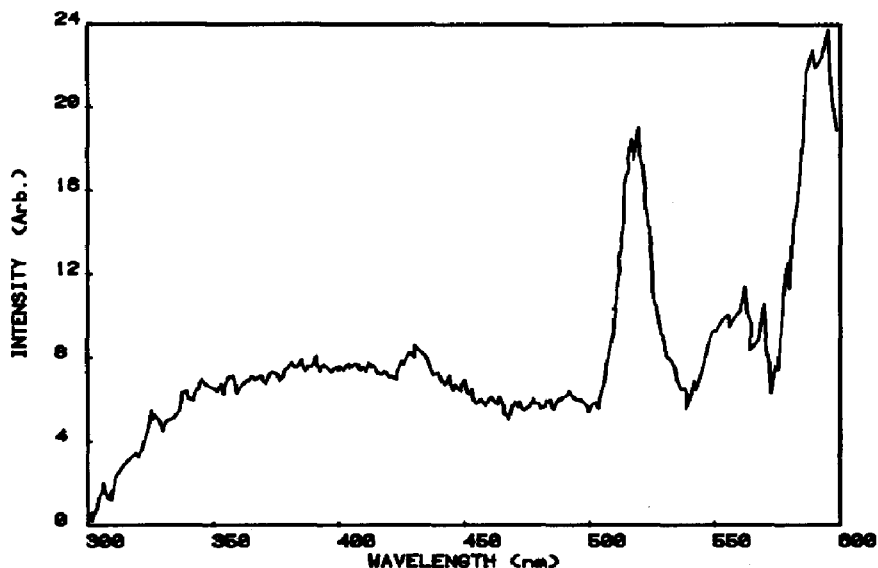


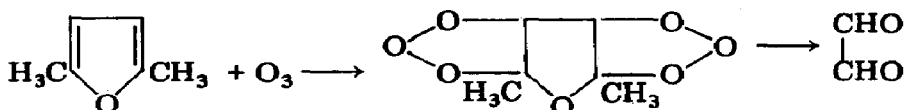
Fig. 3. Chemiluminescence emission from the reaction of ozone with pyrrole (spectral slitwidth, 10 nm; total pressure, 2.2 Torr; ozone, 44 mTorr; pyrrole, 9 mTorr).

was observed. Because of this limitation the emission intensity could not be increased sufficiently to resolve the A_0 and A_1 vibrational progression of CHO bands. However, the emission due to $CH(^2\Delta)$ at 431 nm could still be clearly identified. The OH spectrum was separately recorded with an EMI 9659A photomultiplier tube and is shown in Fig. 4(a); it shows all the prominent peaks due to Meinel bands in addition to those observed in Fig. 3.

Figure 4(b) shows the vibrationally excited OH spectrum observed in the reaction of ozone with 2,5-dimethylfuran. The emission intensity in this case was five times greater than that obtained with pyrrole and therefore all transitions can be clearly identified.

4. Discussion

The reaction of ozone with 2,5-dimethylfuran gives rise to emission from excited formaldehyde and glyoxal. The formation of glyoxal has also been observed in the liquid phase [7] and probably results from the cleavage of the double bonds of the classical valence structure of 2,5-dimethylfuran.



Sufficient evidence for this mechanism has been given in our earlier work [4] where chemiluminescence from the reaction of ozone with furan was studied and only glyoxal emission was observed.

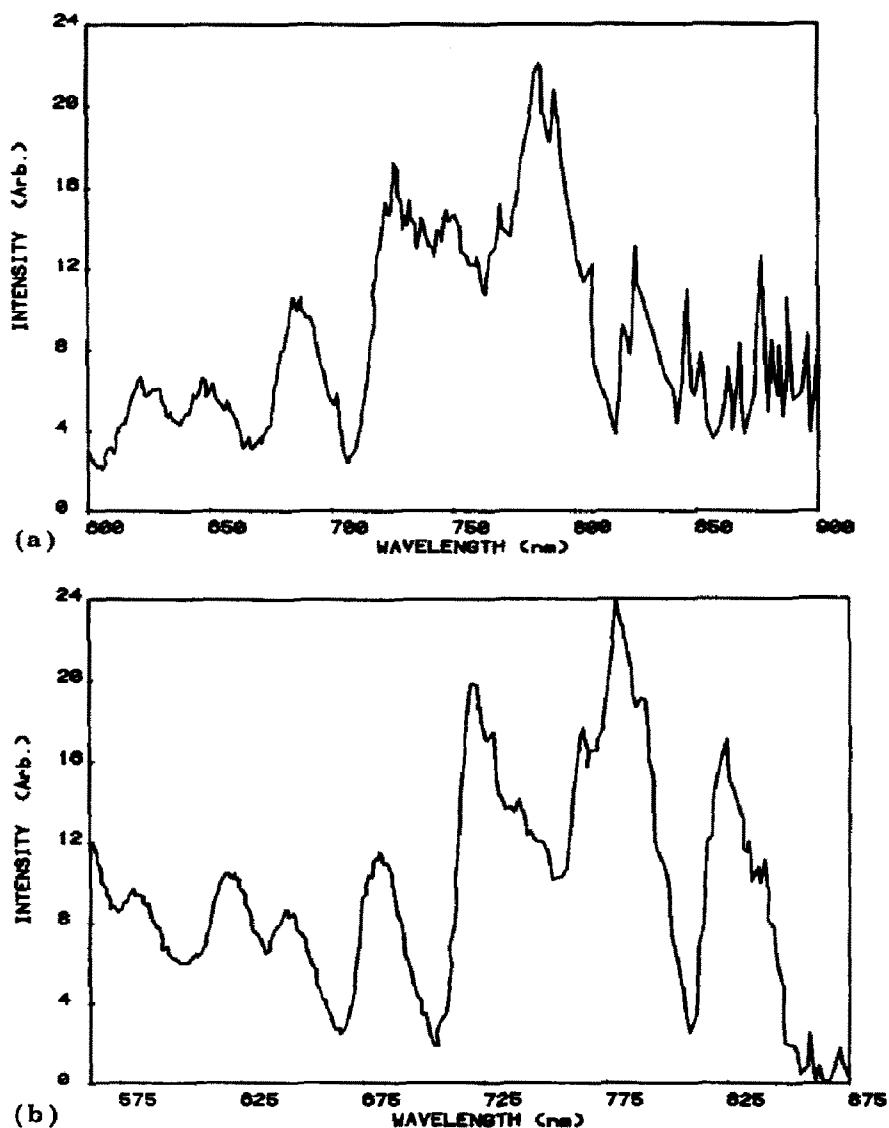
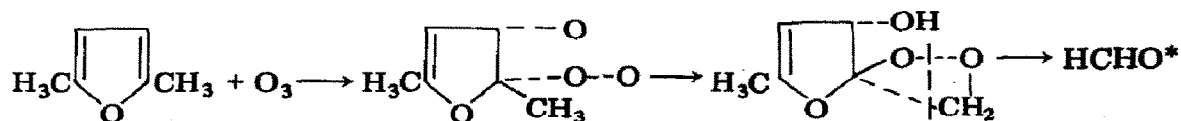


Fig. 4. Chemiluminescence spectrum from the reaction of ozone with (a) pyrrole (spectral slitwidth, 10 nm; total pressure, 1.9 Torr; ozone, 40 mTorr; pyrrole, 8 mTorr) and (b) 2,5-dimethylfuran (spectral slitwidth, 10 nm; total pressure, 3.15 Torr; ozone, 150 mTorr; 2,5-dimethylfuran, 84 mTorr).

Formation of excited formaldehyde takes place via the β -H abstraction pathway of the O'Neal and Blumstein mechanism [8], *i.e.*



Since the formation of 1,2-dioxetanes by ring closure and their decomposition are highly exothermic processes the molecule is expected to have a short

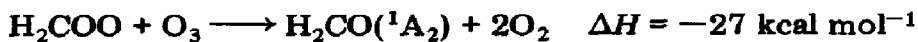
lifetime. O'Neal and Blumstein [8] have estimated $\Delta H_f = -56 \text{ kcal mol}^{-1}$ for the formation of 1,2-dioxetane and $\Delta H_d = -58 \text{ kcal mol}^{-1}$ for its decomposition in the reaction of ozone with 1-butene. Harding and Goddard [9] have estimated $\Delta H_f = -47 \text{ kcal mol}^{-1}$ and $\Delta H_d = -68 \text{ kcal mol}^{-1}$ in the reaction of ozone with ethylene. Bogan *et al.* [10] have studied the chemiluminescent decomposition of dioxetanes formed in the gas phase reaction of $\text{O}_2(^1\Delta_g)$ with a number of vinyl ethers and ethylene and have estimated $\Delta H = -107 \text{ kcal mol}^{-1}$ and $\Delta H = -91 \text{ kcal mol}^{-1}$ respectively. They suggested an upper limit estimate of 10^{-8} s for the lifetime of the dioxetane intermediate in the case of vinyl ethers. They suggested that the formaldehyde spectra observed in their experiments (pressure, 4 Torr; temperature, 625 K) reflect initial excited state populations subject to competition between radiative and non-radiative decay and possibly some collisional relaxation and scrambling. They were also able to observe the vibronic hot band centred at 342 nm.

The formation of 1,2-dioxetanes from the ozonolysis of alkenes in pinacolone and various other ketonic solvents has been reported [11] but the results could not be reproduced. However, the ozonolysis of vinylsilane and its other analogues does result in the formation of 1,2-dioxetanes [11].

The spectrum recorded in this work is quite similar to the spectra observed by Bogan *et al.* [10]. The peak-to-valley ratio is quite small, indicating a high vibrational-rotational temperature. This ratio increases with pressure, indicating that there is a decrease in rotational temperature resulting from collisions. A similar spectrum was also observed in the chemiluminescent reaction between ozone and allene with a very well-characterized emission due to $\text{H}_2\text{CO}(^1\text{A}_2)$ [12]. Shibuya *et al.* [13] have measured the fluorescence quantum yield ϕ_f and the radiative lifetimes for different rotational levels of the 4^1 level of $\text{H}_2\text{CO}(^1\text{A}_2)$. Their $J'K'$ population averaged value $\phi_f = 0.033$ and average radiative lifetime of $3.3 \pm 1.2 \mu\text{s}$ gives a zero-pressure lifetime of 100 ns for the 4^1 level. Shibuya and Lee [14] have also measured the vibrational deactivation rate constant of the 4^1 level by employing various foreign gases and showed that O_2 and argon have a collision efficiency of only 1/5.

Therefore, under the present experimental conditions (pressure, 2.86 Torr; gas composition, 70vol.% O_2 -26vol.%He), the lifetime of the 4^1 level is unaffected by electronic quenching (about 0.005 of gas kinetic collision frequency for O_2) and is less than the effective kinetic collision frequency (time between collisions, 44 ns; collisional efficiency, 1/5). Thus, our chemiluminescence spectrum of H_2CO represents essentially initial populations subject to competition between fluorescence and predissociation. Since the lifetimes (23 ns and 29 ns respectively) of the 4^3 and the 2^14^1 levels are still smaller than the time between collisions they will undergo slight, if any, vibrational relaxation.

Wadt and Goddard [15] have proposed a different mechanism for the formation of excited formaldehyde. They suggested that $\text{H}_2\text{CO}(^1\text{A}_2)$ is formed from the reaction of ozone with the planar $^1\text{A}'(4\Pi)$ state of the Criegee intermediate H_2COO :



Martinez *et al.* [16] have suggested different reaction pathways for the formation of the Criegee intermediate in the reaction of ozone with *trans*-2-butene, tetramethylethylene etc. to explain the formaldehyde fluorescence. However, experiments performed in our laboratory show that the mechanism of Wadt and Goddard may not be responsible for the formation of excited formaldehyde: when we studied the effect of SO₂ on the fluorescence intensity of H₂CO in the reaction of ozone with ethylene and other compounds, we observed no reduction in intensity even when 1 Torr SO₂ was added. This was sufficient to reduce the Criegee concentration by a very large factor (even taking the lowest rate constant of $2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ for the reaction of Criegee with SO₂ [17] and a residence time of 600 ms). Even in the reaction of ozone with 2,5-dimethylfuran, when about 1 Torr SO₂ was introduced into the reaction chamber no change in signal was observed for about 2 min and then the intensity was reduced because of the formation of a yellow coating on the window because of the formation of a complex of SO₂ with 2,5-dimethylfuran.

The source of the OH Meinel bands observed in Fig. 4 is the reaction



It has been suggested that the isomerization and subsequent decomposition of H₂COO provides the source of hydrogen atoms. The intensity of Meinel bands emission in the case of 2,5-dimethylfuran is found to be quite strong compared with that observed in the reaction of ozone with ethylene. This is rather surprising considering the fact that H₂COO is formed much more abundantly in the case of ethylene. It is likely that the formation of vibrationally and/or rotationally hot H₂CO, as indicated by the presence of hot bands, is responsible for the formation of hydrogen atoms. From recent studies on the photolysis of H₂CO at 337 nm employing an N₂ laser, König and Lademann [18] have reported a quantum yield of 0.21 for the reaction H₂CO → H + HCO. This indicates that a large fraction of the hot H₂CO may break up into hydrogen atoms.

The reaction of ozone with furfural gives emission which probably results from the formation of an α-dicarbonyl compound. The half-bandwidth of the peak is nearly 27 nm, which is greater than that of methylglyoxal (20 nm with the same spectral slitwidth [1, 2]). Since methylglyoxal emission exhibits an emission band broader than that of glyoxal, more highly substituted α-dicarbonyls may be expected to have a peak broader than that of methylglyoxal. The appearance of a weak shoulder to the main peak, similar to that in methylglyoxal phosphorescence, is further support that it is an α-dicarbonyl emission. At present it is difficult to propose a mechanism, but the attack of ozone probably takes place on the double bond at which the H—C=O group is attached. The weak emission intensity, observed only at high pressures, is probably due to slow attack of ozone on the electron-deficient double bond of furfural.

The reaction of ozone with pyrrole leads to the formation of excited glyoxal via a pathway similar to that proposed in the case of furan and 2,5-dimethylfuran. No formaldehyde fluorescence was observed, owing to the absence of a methyl group as in the case of furan [4]. The other emission observed is from excited CHO and CH($^2\Delta$) radicals. They are probably formed from the fragmentation of the molecule. A similar spectrum was observed by Hansen and Pitts [19] in the chemiluminescent reaction of ozone with C₂H₂ in which emission from CHO, CH and OH($^2\Sigma^+$) was identified. Fragmentation of the molecule may also be responsible for the formation of hydrogen atoms in the system which give rise to Meinel band emission.

References

- 1 P. K. Arora and K. G. Vohra, *Chem. Phys. Lett.*, **96** (1983) 161.
- 2 P. K. Arora, J. P. S. Chatha and K. G. Vohra, *Chem. Phys. Lett.*, **100** (1983) 93.
- 3 P. K. Arora and J. P. S. Chatha, *Can. J. Chem.*, **62** (1984) 417.
- 4 P. K. Arora, *J. Photochem.*, **27** (1984) 1.
- 5 W. A. Kummer, J. N. Pitts, Jr., and R. P. Steer, *Environ. Sci. Technol.*, **5** (1971) 1045.
- 6 J. P. S. Chatha, P. K. Arora, Nalini Raja and P. B. Kulkarni, *Indian J. Technol.*, **19** (1981) 300.
- 7 P. S. Bailey, *Chem. Rev.*, **58** (1958) 925.
- 8 H. E. O'Neal and C. Blumstein, *Int. J. Chem. Kinet.*, **5** (1973) 397.
- 9 L. B. Harding and W. A. Goddard, *J. Am. Chem. Soc.*, **100** (1978) 7180.
- 10 D. J. Bogan, J. L. Durant, Jr., R. S. Sheinson and F. W. Williams, *Photochem. Photobiol.*, **30** (1979) 3.
- 11 K. R. Kopecky, in W. Adams and G. Clinto (eds.), *Chemically and Biologically Produced Excited States*, Academic Press, New York, 1982, p. 101.
- 12 S. Toby, *J. Lumin.*, **8** (1973) 94.
- 13 K. Shibuya, P. W. Fairchild and E. K. C. Lee, *J. Chem. Phys.*, **75** (1981) 3397.
- 14 K. Shibuya and E. K. C. Lee, *J. Chem. Phys.*, **69** (1978) 758.
- 15 W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97** (1975) 3004.
- 16 R. I. Martinez, J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, **103** (1981) 3807.
- 17 J. T. Herron, R. I. Martinez and R. E. Huie, *Int. J. Chem. Kinet.*, **14** (1982) 201.
- 18 R. Konig and J. Lademann, *Chem. Phys. Lett.*, **94** (1983) 152.
- 19 D. A. Hansen and J. N. Pitts, Jr., *Chem. Phys. Lett.*, **35** (1975) 569.