Time-resolved fluorescence of NO_2 in a magnetic field

S.A. Nizkorodov [1], V.I. Makarov [2], I.V. Khmelinskii
Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russian Federation

S.A. Kotschubei and K.A. Amosov
Institute of Semiconductor Physics, 630090 Novosibirsk, Russian Federation

Received 12 January 1993, in final form 4 October 1993

The influence of a magnetic field on the fluorescence of NO_2 has been studied by time-resolved experiments It has been found that the magnetic field quenched the pre-exponential of the fluorescence signal but did not alter its lifetime A simple model based on an expanded two-level approximation has been proposed The model has qualitatively accounted for the observed experimental results

1. Introduction

Spectroscopy of NO_2 in the visible region is greatly complicated [1–6] since the two existing absorbing electronic states $^2B_1$ and $^2B_2$ heavily perturb each other The perturbation causes mixing of rovibronic levels belonging to those electronic states which substantially complicates not only the absorption and fluorescence spectra of the molecule but also the radiationless relaxation dynamics in a given electronic system [7–10]

It has long been known that perturbation by an external magnetic field may serve as a source of additional channels of radiationless relaxation of electronic excitation energy in some molecules [11–17] The direct consequence of this is that magnetic fields may have a definite influence on the molecules' absorption cross-section, quantum yield of fluorescence, spectral distribution of the latter, etc On the other hand, studying magnetically induced quenching of fluorescence for various molecular systems may provide valuable information about mechanisms of radiationless relaxation Investigation of the magnetic quenching of time-resolved fluorescence of small and medium-sized molecules has turned out to be the most powerful tool for elucidating the nature of magnetically induced radiationless transitions since it is the fluorescence lifetime that is most sensitive to a perturbation of that kind

As was first demonstrated in experiments with stationary excitation of fluorescence by Levy et al [18–20], the fluorescence and absorption of nitrogen dioxide are quenched in the presence of a magnetic field It was shown that the magnetic field affected only the discrete structure of the fluorescence spectrum [19] but not the dense, unresolved manifold The magnitude of the magnetic field effect depended Lorentzianally on the magnetic field strength Pressure dependence of the effect was observed only for low gas density Finally, excitation wavelength dependence of the effect was found to be strongly irregular [20] The observed data were qualitatively accounted for by the model which assumed a magnetically induced coupling of the levels of the fluorescent state $^2B_1$ with highly excited levels of the ground $^2A_1$ state [20–22] The model reduced actually to an analysis of a two-level system coupled by magnetic field perturbation

To gain a better understanding of the mechanism of magnetically induced quenching of NO_2 fluorescence we have studied the influence of magnetic fields

---

[1] Present address Institute of Physical Chemistry, Universitat Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

[2] Present address Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako-shi, Saitama 351-01, Japan

on the time-resolved fluorescence of NO_2. In addition, we have performed a simple theoretical treatment of our experimental results on the basis of an expanded two-level approximation.

2. Experimental

The experiment was carried out in a cylindrical stainless-steel gas cell (d=40 mm, l=100 mm) equipped with two hole-centered solenoids creating a uniform magnetic field in the working volume and six quartz windows placed along the three mutually perpendicular axes of the cell. The strength of the field could be smoothly varied from 0 to 3.6 kG. The pressure in the cell was typically 10^{-3}–10 Torr.

The fluorescence of pure gaseous nitrogen dioxide was excited perpendicularly to the magnetic field by a pulsed home-built dye laser pumped with a XeCl excimer laser. The dye laser (coumarin 120 in ethanol) was designed with the use of an oscillator–amplifier scheme with transverse pumping. The laser bandwidth was 0.15 cm^{-1} (at 436 nm), the energy was 3–5 mJ/pulse, the pulse duration was ≈10 ns. The diameter of the beam was 3 mm. The fluorescence was observed with two photomultipliers, placed in perpendicular and parallel directions with respect to the magnetic field and perpendicularly to the beam of exciting light. We used two photomultipliers to find out if the quenching effect of the magnetic field was caused by the field itself or just by possible alteration of the spatial distributions of the fluorescence in the field. Both sets of measurements gave the same results indicating that the latter was not the case. In front of each photomultiplier we put 700 nm interference filters to prevent scattering of the exciting light.

Data acquisition was performed by a microcomputer linked with a multichannel analyzer, a boxcar and other devices through a CAMAC interface. The multichannel analyzer had 1024 8-bit memory cells and a sample rate ranging from 50 to 3200 ns/count. Time-resolved fluorescence emerging from the cell after a dye laser pulse was recorded by the analyzer, normalized by laser power, averaged and treated in the computer. Experiments with an empty cell gave no background.

The NO_2 used in our experiments was obtained by thermal decomposition of $Pb(NO_3)_2$ and purified by vacuum trap-to-trap distillation to remove traces of NO and O_2.

3. Results

In agreement with data determined by other workers [14,23] we found that the fluorescence signal of NO_2 at $\lambda_{ex}=436.45$ nm was essentially monoexponential. Analysis of the Stern–Volmer dependence gave us the values of the radiative lifetime $\tau_f^0=36\pm6$ µs and the self-quenching rate constant $k_1=(1.73\pm0.14)\times10^{-11}$ $cm^3\,s^{-1}$ for NO_2 fluorescence. These are in good agreement with the data of ref. [23] (for $\lambda_{ex}=434.80$ nm).

We found that the magnetic field decreased the amplitude of NO_2 fluorescence (the pre-exponential parameter) but had no influence on its lifetime. Fig. 1 shows the ratio (A_H/A_0)=MFE (magnetic field effect) versus magnetic field strength (H) at an NO_2 pressure of 0.14 Torr and $\lambda_{ex}=436.45$ nm. Here A_H, A_0 are the signal amplitudes measured with and without magnetic field, respectively. The qualitative behaviour of this curve agrees with the data of refs. [18–20], namely it can be fitted by the Lorentzian law. It should be noted, however, that since we used a different excitation wavelength and experimental methodology than those in refs. [18–20] our comparison with their results must bear only a qualitative character.

Fig. 2 shows the dependence of the MFE on NO_2

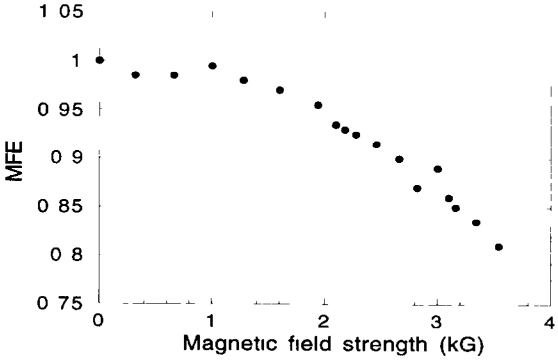

Fig. 1. Dependence of the MFE (magnetic field effect=A_H/A_0) on magnetic field strength (H) at a gas pressure of 0.14 Torr and $\lambda_{ex}=436.45$ nm.

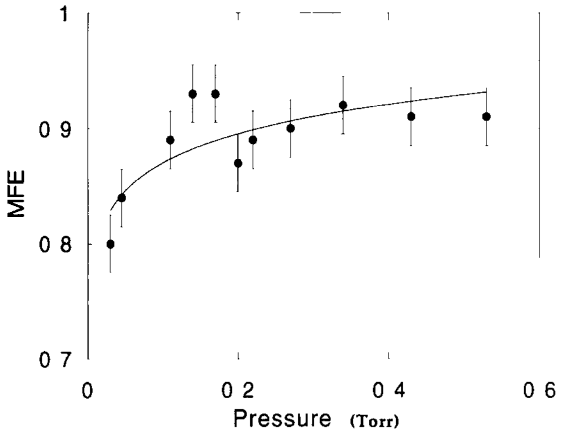

Fig 2 MFE versus gas pressure at $H=2$ 7 kG and $\lambda_{ex}=436$ 45 nm

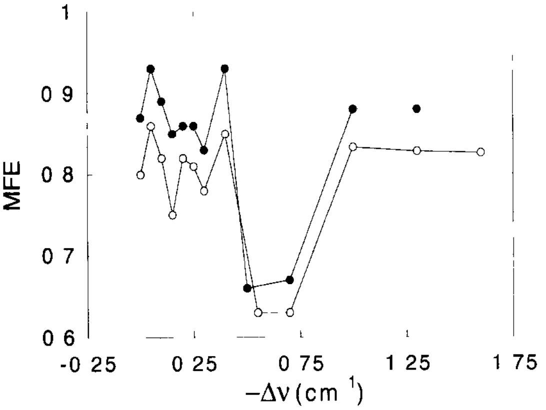

Fig 3 MFE versus excitation energy at $H=2$ 7 kG and at two different gas pressures (●) 0 29 Torr and (○) 0 03 Torr Zero on the x axis corresponds to 436 45 nm

pressure, equal to the total gas pressure (p), at $\lambda_{ex}=$ 436 45 nm and $H=2$ 7 kG One can see that at low pressure the magnitude of the magnetic field effect decreased with pressure (the MFE became closer to 1) whereas at higher pressures it remained unchanged within experimental accuracy A similar behavior of such a dependence was observed in ref [20]

Fig 3 shows the dependence of the MFE on λ_{ex} at $p=0$ 29 and 0 03 Torr, $H=2$ 7 kG The dependence is irregular, as in ref [20]

4. Discussion

Radiation with $\lambda_{ex}=436$ 45 nm excites transitions $^2B_1 \leftarrow {}^2A_1$ and $^2B_2 \leftarrow {}^2A_1$ in NO_2 [1-10,24] Unfortunately, detailed rotational analysis of NO_2 absorption in this spectral region has not been published yet and so we do not know which rovibronic levels were excited in our case Since two electronic transitions were involved in absorption one could expect to get bi- or poly-exponential fluorescence decay rather than the experimentally observed monoexponential one The reason for this may be due to a small or on the contrary a large difference in the lifetimes of the $^2B_1$ and $^2B_2$ electronic states In both cases the detection of biexponentiality may be difficult

NO_2 is a sparse intermediate case molecule [25] at our range of excitation energy, i e $\gamma_\ell \rho_\ell \approx 0$ 1 < 1 Here γ_ℓ and ρ_ℓ are the linewidth and density of rovibronic ground state levels interacting with the excited state levels Therefore, in non-collisional conditions, the quantum yield of NO_2 fluorescence should be close to 1 However, at finite gas pressure there always exists some collisional relaxation which tends to reduce the yield If the levels of the excited states interact with those of the ground state such a collisional relaxation would result in fluorescence quenching [25] (the interaction may be induced by the collision itself or may have an intramolecular origin)

The external magnetic field may couple the levels of the $^2B_1$ electronic state and of the ground $^2A_1$ state of NO_2 [26-28] It was shown experimentally in this work and by Levy et al [18-20] that the magnetic field suppressed fluorescence of this molecule The authors of refs [18-20] proposed a kinetic model which in the steady-state treatment for NO_2^* accounted for the experimental results obtained at stationary excitation of fluorescence The kinetic scheme adopted a formal rate constant for the process of "magnetically collisionally induced fluorescence quenching" which was taken to be proportional to H^2 However, this model implied a shortening of the NO_2 fluorescence lifetime in the magnetic field which we did not observe Thus, Levy's treatment does not account for our experimental results

For sparse intermediate case molecules especially, a simple model can be developed on the basis of a two-level approximation [28] The model considers fluorescence of a molecule as a sum of individual emissions from a number (N) of coherently excited two-level systems, with each such system being composed of one ground state level (ℓ) and one fluorescent state level (s) Let us denote $|\mathrm{s}^i\rangle$ and $|\ell^i\rangle$ zeroth-order eigenfunctions corresponding to s and ℓ levels in couple number i The magnetic field perturbation will mix eigenfunctions inside each couple, and the degree of mixing will be determined by the magnetic field strength and by the difference in zeroth-order energies New wavefunctions will have the following form

$$|n^i\rangle = \sum_n \alpha_n^i |\mathrm{s}^i\rangle + \beta_n^i |\ell^i\rangle , \quad n=1,2 , \tag{1}$$

new energies will be ϵ_n^i and new widths will be

$$\gamma_n^i = \gamma_\mathrm{s}^i |\alpha_n^i|^2 + \gamma_\ell^i |\beta_n^i|^2 \tag{2}$$

Here α_n^i, β_n^i and ϵ_n^i can easily be evaluated from first-order perturbation theory Coherent excitation will excite both $|1^i\rangle$ and $|2^i\rangle$ levels in each couple The state initially prepared by laser excitation can be written as a linear combination,

$$|\Psi(t)\rangle = \sum_i^N \sum_n^2 c_n^i |n^i\rangle \exp(-\mathrm{j}E_n^i t) ,$$

$$\mathrm{j}^2 = -1 , \tag{3}$$

$$E_n^i = \epsilon_n^i - 0.5\,\mathrm{j}\gamma_n^i \tag{4}$$

Experimentally observed fluorescence should be proportional to the sum

$$I_\mathrm{fl}(t) \propto \sum_i^N (\tau_\mathrm{s}^i)^{-1} \langle \mathrm{s}^i | \Psi(t)\rangle^2 \tag{5}$$

The (oversimplified) model assumes that the couples differ from each other only in the energy gap $\Delta\omega$ between the levels comprising the couple while the coupling matrix element V_H, pressure-dependent linewidths γ_s and γ_ℓ, and radiative lifetime of zeroth-order (s) state τ_s are the same for all the couples Let us rewrite assumption (5) as

$$I_\mathrm{fl}(t) \propto \tau_\mathrm{s}^{-1} \sum_i^N \left[\left(\sum_n^2 c_n^i \langle \mathrm{s}^i | n^i \rangle \exp(-\mathrm{j}E_n^i t) \right)^2 \right] \tag{6}$$

The quantity in square brackets is the fluorescence decay of a single couple which is a complicated function of V_H, γ_s, γ_ℓ and $\Delta\omega$ The summation of the contributions to total fluorescence signal from individual couples is then replaced by integration over $\Delta\omega$ Such a procedure is correct only if the number of two-level systems involved is quite large Computer simulations showed, however, that the basic features of the model already became apparent when only three couples with different $\Delta\omega$ were included in the sum The result is that the fluorescence signal in a magnetic field may be approximately separated into several monoexponential components The first one is a fast component which reflects the process of dephasing of coherently excited levels interacting with the magnetic field, $\gamma_\mathrm{fast} \propto V_H^2$ The lifetime of a short-lived component must be of the order of picoseconds [29,30] so it could not be resolved under our experimental conditions The other components should have lifetimes of the order of γ_ℓ^{-1} and γ_s^{-1} As far as long-lived components are concerned the result of the integration over $\Delta\omega$ again gives us a single-couple decay where $\Delta\omega'$ is replaced by some average quantity close to $\langle\omega\rangle = \sqrt{\langle\Delta\omega^2\rangle}$ Thus we can find an analytical representation of long-lived fluorescence decay in the field of perturbation V_H for such a special case

To apply this model to NO_2 the following assumptions should be made

(a) The magnetic field induces the mixing of the levels of two Renner–Teller components $^2A_1$ and $^2B_1$ of the $^2\Delta_g$ state of the linear NO_2 molecule The mechanism was described in detail in refs [26–28]

(b) The linewidths of the levels of the fluorescent (s) and ground (ℓ) states can be written as $\gamma_\mathrm{s} = \tau_\mathrm{s}^{-1} + k_\mathrm{s} p$ and $\gamma_\ell = \tau_\ell^{-1} + k_\ell p$ where k_s and k_ℓ are the collisional relaxation rate constants and p is the gas pressure The meaning of the τ_ℓ^{-1} term in the expression for γ_ℓ may be understood as follows Rotational levels of NO_2 with given J are split by spin–rotational interaction into two components F_1 and F_2 Each of them is in turn split into three components G_i by hyperfine interaction The constants of the spin–rotational and hyperfine interactions for the ground state of NO_2 are 500 and 143 MHz, respectively [31] If we assume that the cross sections of collisional relaxation among the components of hyperfine and fine structure are much larger than $\sigma_{\mathrm{s},\ell}$ and γ_G^i widths exceed the values of hyperfine and fine splitting then formally the relaxation rate in these subsystems will be described by unimolecular kinetics.

(c) The effective density of the ground state rovibronic levels seen by *one* fluorescent state level (s) is $\rho_\ell \approx 0.6$ cm. Here selection rules $\Delta K=0$ and $\Delta J=\pm 1, 0$ for the magnetic field coupling between the levels of the $^2A_1$ and $^2B_1$ states [26–28] were taken into consideration.

(d) The maximum value of the matrix element of the field-induced interaction is not greater than 0.1 cm^{-1}/kG [28]. Since $\rho_\ell \approx 0.6$ cm we take into account only occasional two-level resonances [25]. (The two-level approximation is applicable only when $V_H \ll (\rho_\ell)^{-1}$. If this condition is violated three-, four-, etc. level interactions must be considered.)

(e) Compared to the ρ_ℓ value the density of optical transitions in NO_2 molecule is large enough [31] so that a 0.15 cm^{-1} wide excitation populates a great number ($\geqslant 10^3$) of rovibronic levels. NO_2 fluorescence may be thought of as a superposition of the emission of that number of individual levels, some of which are coupled with other levels via the magnetic field interaction.

Let us now proceed to discuss our experimental results within the frame of the outlined model. Since the NO_2 fluorescence lifetime was independent of magnetic field strength in the 0.01–2 Torr pressure range we have to accept

$$\gamma_s \approx \gamma_\ell \; (=\gamma), \quad k_s \approx k_\ell \; (=k_q) \tag{7}$$

Besides, τ_s and τ_ℓ should have the same order of magnitude. No experimental information about k_ℓ values is available in the scientific literature so we can take the value $k_s = (1.73 \pm 0.14) \times 10^{-11}$ cm^3 s^{-1} as some integral characteristic of k_ℓ. Assumption (7) automatically gives monoexponential fluorescence decay in a magnetic field with rate γ and a pre-exponential parameter equal to

$$A_H = \frac{4V_H^2 + 2\langle\omega\rangle^2}{2(\langle\omega\rangle^2 + 4V_H^2)} \tag{8}$$

(The high-frequency oscillatory part that should have averaged down to zero in our experiment was neglected.) Thus we have a Lorentzian shape for normalized MFE,

$$\mathrm{MFE}^* = \frac{A_H - A_\infty}{A_0 - A_\infty} = \frac{1}{1 + \mathrm{const}\; V_H^2},$$

$$\mathrm{const} = 4/\langle\omega\rangle^2, \tag{9}$$

in agreement with the experimental results of ref. [20]. Unfortunately, we did not saturate the MFE in our experiments but our data still obey eq. (9). In the limit of low fields $A_H/A_0 = 1 - \mathrm{const}\,(1 - A_\infty/A_0) V_H^2$ and one can see from fig. 4 that experimental points $(1 - A_H/A_0)$ are indeed directly proportional to H^2. From the slope of this dependence we can estimate an upper limit for the coefficient of proportionality χ between V_H and H, $V_H = \chi H$. Even if $\langle\omega\rangle$ is as large as 0.1 cm^{-1} χ has the order of 10^{-2} cm^{-1}/kG. This validates assumption (d).

Consider now an application of the density-matrix formalism to the problem. The solution of the characteristic equation for a two-level system shows that the presence of a perturbation will change the effective radiative lifetime of the system as far as $\gamma_s \neq \gamma_\ell$, i.e. we again have to accept that eq. (7) holds. For the case of stationary excitation one can obtain the following expression for the intensity of fluorescence from a single couple

$$I_{fl} = W_0 \tau_s^{-1} \frac{2\Gamma V_H^2 + \gamma_\ell(\Delta\omega^2 + \Gamma^2)}{\gamma_s \gamma_\ell(\Delta\omega^2 + \Gamma^2) + 4\Gamma^2 V_H^2} \tag{10}$$

Here W_0 is the rate of optical pumping of level s by a cw laser, $\Gamma = \frac{1}{2}(\gamma_s + \gamma_\ell)$. When N two-level systems are excited the total emission can be written out as a sum of (10),

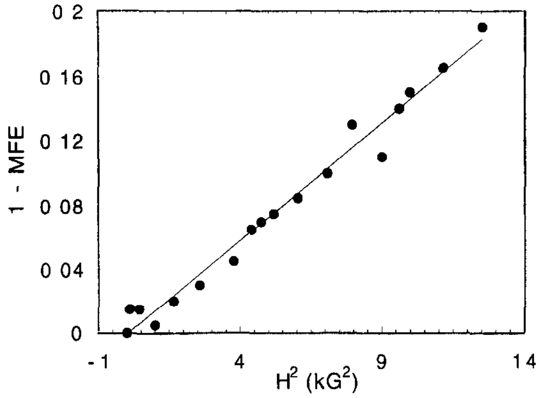

Fig. 4. Linear dependence of (1-MFE) on the squared magnetic field strength. The slope of the dependence is equal to 0.015.

$$I_{\mathrm{fl}} \propto \sum_{i}^{N} (I_{\mathrm{fl}}^{i})\alpha_i \,, \qquad (11)$$

where α_i is the statistical weight of the ith two-level system Let us assume for simplicity a square excitation profile Since all the couples are identical besides having different $\Delta\omega$ we can state that $\alpha_i = 1/N$ Summation (11) will explicitly replace $\Delta\omega$ in (10) by $\langle\omega\rangle$ Again the expression for normalized MFE

$$\mathrm{MFE}^* = \frac{I_{\mathrm{fl}} - I_{\mathrm{fl}}^{\infty}}{I_{\mathrm{fl}}^{0} - I_{\mathrm{fl}}^{\infty}} = \frac{1}{1 + \mathrm{const}\ V_H^2} ,$$

$$\mathrm{const} = \frac{4}{\langle\omega\rangle^2 + \Gamma^2} \qquad (12)$$

takes a Lorentzian shape Note that this is the same result as eq (9) if one assumes in eq (12) that $\langle\omega\rangle \gg \Gamma$

Now let us inspect the pressure dependence of the MFE given by eq (10) Substituting (7) into (10) we obtain

$$\mathrm{MFE} = \frac{I_{\mathrm{fl}}}{I_{\mathrm{fl}}^{0}} = 1 - \frac{2V_H^2}{\langle\omega\rangle^2 + (\tau^{-1} + k_{\mathrm{q}} p)^2 + 4V_H^2} \qquad (13)$$

Here τ has the same order of magnitude as τ_{s} and τ_{ℓ} This predicts a decreasing MFE (i e approaching unity) with pressure at low pressures, when $k_{\mathrm{q}} p$ is of the same order of magnitude as $\langle\omega\rangle^2$ and/or V_H^2, and saturation of the effect at MFE$\approx$1, when the pressure term becomes the major one in the denominator This is in good agreement with the data of Levy et al [18–20] and with our experimental results Note that I_{fl} vanishes at infinitely large pressure in accordance with intuitive expectation

The dependence of the MFE on excitation wavelength can be understood if we remember that the real density of both s and ℓ states is not uniform The average value of the perturbation matrix element must be different from one set of levels to another as well Therefore contamination of the resulting wavefunction with ℓ levels will depend on the excitation wavelength For example, a sharp increase in the effect at $-\Delta\nu \approx 0$ 6 cm^{-1} may testify to a much stronger field-induced s–ℓ mixing at this point than at say $\Delta\nu = 0$

Thus using the assumptions made and the model developed in ref [28] we are able to explain qualitatively our experimental results

References

[1] C G Stevens and R N Zare, J Mol Spectry 56 (1975) 167
[2] J C D Brand, W H Chan and J L Hardwick, J Mol Spectry 56 (1975) 309
[3] N Sugimoto, J Mol Spectry 106 (1984) 307
[4] J C D Brand and P H Chiu, J Mol Spectry 75 (1979) 1
[5] N Sugimoto, S Takezawa and N Takeuchi, J Mol Spectry 102 (1983) 372
[6] N Sugimoto, N Takeuchi and S Takezawa, Chem Phys Letters 99 (1983) 475
[7] J C D Brand, J L Hardwick, R J Pirkle and C J Seliskar, Can J Phys 51 (1973) 2184
[8] J L Hardwick and J C D Brand, Chem Phys Letters 21 (1973) 458
[9] V M Donnelly and F Kaufman, J Chem Phys 66 (1977) 4100
[10] V M Donnelly and F Kaufman, J Chem Phys 69 (1978) 1456
[11] V I Makarov and I V Khmelinskii, Chem Phys 146 (1990) 1
[12] J H Van Vleck, Phys Rev 40 (1932) 544
[13] M Lombardy, R Jost, C Michel and A Trammer, Chem Phys 46 (1980) 273
[14] H Watanabe, S Tsuchiya and S Koda, J Phys Chem 87 (1983) 906
[15] H Watanabe, S Tsuchiya and S Koda, J Chem Phys 82 (1985) 5310
[16] H Watanabe, Y Hyodo and S Tsuchiya, J Phys Chem 86 (1982) 685
[17] Y Matsumoto, H Spangler and D W Pratt, Chem Phys Letters 85 (1983) 343
[18] S Butler, C Kahler and D H Levy, J Chem Phys 62 (1975) 815
[19] R Solarz, S Butler and D H Levy, J Chem Phys 58 (1973) 5172
[20] S Butler and D H Levy, J Chem Phys 66 (1977) 3538
[21] S H Lin and Y Fujimura, Excited States 4 (1979) 237
[22] P R Stannard, J Chem Phys 68 (1978) 3932
[23] K O Patten, J D Burley and H S Johnston, J Phys Chem 94 (1990) 7960
[24] G D Gillispie, A V Khan, A C Wahl, R P Hosteny and M Krauss, J Chem Phys 63 (1975) 3425
[25] K F Freed, Advan Chem Phys 42 (1980) 207
[26] J C D Brand, J L Hardwick, D R Humphrey, Y Hamada and A J Merer, Can J Phys 54 (1976) 186
[27] R Kullmer and W Demtroder, J Chem Phys 83 (1985) 2712
[28] V I Makarov and I V Khmelinskii, J Photochem Photobiol A 69 (1992) 7
[29] F Lahmanni, A Trammer and C Tric, J Chem Phys 60 (1974) 4431
[30] K.A Amosov, S A Kotschubei, K N Naumochkin, V I Makarov, I V Khmelinskii and N M Bazhin, Chem Phys 171 (1993) 275
[31] K K Lehmann and S L Coy, J Chem Phys 87 (1985) 3290