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Citation: The Journal of Chemical Physics **95**, 2259 (1991); doi: 10.1063/1.460982 View online: http://dx.doi.org/10.1063/1.460982 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/95/4?ver=pdfcov Published by the AIP Publishing

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# Radiative lifetimes and reactivity of metastable NO<sup>+</sup>( $a^{3}\Sigma^{+}, v$ ) and O<sub>2</sub><sup>+</sup>( $a^{4}\Pi_{u}, v$ )

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(Received 26 December 1990; accepted 30 April 1991)

The radiative lifetimes and reactivity of metastable NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) and O<sub>2</sub><sup>+</sup> ( $a^{4}\Pi_{u}$ ) have been investigated using a triple cell ion cyclotron resonance (ICR) spectrometer. Radiative lifetimes of (100 ± 20) ms and (135 ± 25) ms have been found for NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ )  $v \ge 1$  and  $v \ge 0$ respectively, with Ar and CO<sub>2</sub> as monitor gases. The overall reaction rate of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ,  $v \ge 1$ ) with Ar ( $6.5 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>) is 1 order of magnitude larger than the rate of v = 0 determined in flowing afterglows. CO<sub>2</sub> reacts at collision rate. For O<sub>2</sub><sup>+</sup> the overall lifetime of  $v \ge 0$ , determined with Ar as monitor, is ( $30 \pm 6$ ) ms in between the two values (7 and 130 ms) found by Bustamente *et al.* using the photodissociation technique. The possible reasons for the longer lifetimes determined in previous ICR experiments is discussed. In the absence of any *ab initio* calculation, the experimental results on NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) may only be compared to values calculated using an approximated perturbation model. Unfortunately, the reliability of this model, also used in the previous studies, is very limited because of the large uncertainty on the coupling between the metastable  $a^{3}\Sigma^{+}$  and the perturbing radiative  $A^{-1}\Pi$  states.

# I. INTRODUCTION

Since transition from the first excited state to the ground state is spin forbidden for both NO<sup>+</sup> and  $O_2^+$ , these states are expected to be long lived and to be able to undergo reactions which are endothermic with the ground state ions.

Reactivity of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) and O<sub>2</sub><sup>+</sup> ( $a^{4}\Pi_{u}$ ) with various molecules has been studied in flow tube experiments at 0.04–2.5 eV kinetic energies.<sup>1-4</sup> Ion beam experiments have been performed with 0.8 to 3 keV NO<sup>+ 5</sup> and also with state selected NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ , v and  $b^{3}\Pi$ , v) at low kinetic energies.<sup>6</sup>

The flow tube experiments indicate that the lifetimes must be longer than a few milliseconds, and, as a consequence, cannot be measured by spectroscopic methods.

Two types of experimental methods have been used to determine the lifetimes.

—Laser induced (pre)dissociation as a function of storage time in an octopole ion trap<sup>7</sup> and chemical reactivity as a function of storage time in an ion cyclotron resonance (ICR) cell with Fourier transform (FT) detection of the ions.<sup>8.9</sup>

Unfortunately, the different results are not in very good agreement. For  $O_2^+$  ( $a^4\Pi_u$ ), the photodissociation technique<sup>7</sup> gives 7 and 130 ms assigned, respectively, to the  $F_1, F_4$  and  $F_2, F_3$  spin components.

The FT-ICR experiments performed with two different experimental procedures give two different sets of values:

for  $O_2^+$   $(a \,{}^4\Pi_u)$ :  $\tau = 220 \,{}^{+30}_{-20} \,\text{ms}^8$  and  $\tau = 101 \,{}^{+7}_{-6} \,\text{ms}^9$ for NO<sup>+</sup>  $(a \,{}^3\Sigma^+)$ :  $\tau = 1450 \,{}^{+1150}_{-450} \,\text{ms}^8$  and  $\tau = 530 \,{}^{+300}_{-100} \,\text{ms}^9$ 

This is why we decided to reinvestigate these ions using a technique which proved to be quite successful to determine the lifetimes of vibrationally excited ground state ions like NO<sup>+</sup>  $(X,v = 1-4)^{10,11}$  or H(D)Cl<sup>+</sup> (X,v = 1).<sup>12</sup>

### **II. EXPERIMENTAL**

As the experimental procedure has already been described,<sup>11,13</sup> only a brief summary and details pertinent to the present experiment are given here.

The Orsay triple cell ICR spectrometer<sup>13</sup> consists of three differentially pumped ICR cells communicating through two ion funnels acting as conductance limits. Ions are produced in the first cell with a 40 to 70 eV pulsed electron beam. They are drifted in about 0.5 ms into the second cell (relaxation cell) where they can be stored for variable times (1 to 150 ms). Differential pumping maintains a very low pressure in this cell. In the third cell the ions react with the monitor gas at constant pressure and reaction time. Finally, the reactant and product ions are drifted back into the low pressure cell where they are detected using an IonSpec Fourier Transform data system.

To obtain radiative decays, the residence time of the ions of interest is varied in the relaxation cell, a section of the machine where collisions are negligeable. As long as all the other parameters are kept constant during an experiment (ion production, ion monitoring, and ion detection) the variation of the monitor ion intensity reflects only the processes occurring in the relaxation cell. In particular, even if only a fraction of the excited state is converted into monitor ions in the reaction cell (slow monitor reaction, or competing reaction(s), or partial collisional deactivation) the method is still valid as long as the conversion stays constant, which is the case since the monitor gas pressure and the reaction time are kept constant.

This way, ion production, radiative relaxation and reaction processes are separated, "in space" and "in time" in this differentially pumped multichamber experiment, while they are separated in time only in the pulsed valve single cell device used at UCSB.<sup>14</sup> In both experiments, the observed decays are due to radiative processes in first approximation, but have to be corrected for the minor contribution of the

J. Chem. Phys. 95 (4), 15 August 1991 131, 110021 9606/91/162259-06\$03.00, 06:15. © 1991 American Institute of Physics 2259

<sup>&</sup>lt;sup>a)</sup> Associated with CNRS.



FIG. 1. Calculated potential energy curves for NO  $^+$  taken from Ref. 19. The dashed lines show the ionization potential of the monitor gases.

competing reaction and/or collisional deactivation occurring with the background gas during the relaxation time. While pressure time profiles are difficult to assess in pulsed gas experiments, this correction is easy to make in the triple cell machine where the pressures are static and can be measured. The background pressure in the relaxation-detection cell is typically  $\sim 5 \times 10^{-8}$  Torr, mainly H<sub>2</sub>O, in addition to  $\sim P_1/150$  of parent gas leaking from the source and  $\sim P_3/150$  of monitor gas leaking from the reaction cell. The corresponding corrections are usually of the order of 20% for lifetimes around 100 ms.

# III. NO<sup>+</sup>( $a^{3}\Sigma^{+}$ )

# A. Vibrational distribution of NO<sup>+</sup>( $a^{3}\Sigma^{+}$ )

Ionization of ground state NO by 70 eV electrons produces NO<sup>+</sup> in a number of singlet and triplet bound electronic states:  $X^{1}\Sigma^{+}$ ,  $a^{3}\Sigma^{+}$ ,  $b^{3}\Pi$ ,  $W^{3}\Delta$ ,  $b'^{3}\Sigma^{-}$ ,  $A'^{1}\Sigma^{-}$ ,  $W^{1}\Delta$ , and  $A^{1}\Pi$  (Fig. 1). All the excited states, except  $a^{3}\Sigma^{+}$ , have radiative lifetimes shorter than the minimum time required to drift the ions from the source to the relaxation cell. The longer measured lifetime is 135  $\mu$ s for  $b^{3}\Pi$ .<sup>15</sup> Recent calculations<sup>16</sup> indicate some longer lifetimes for the  $W^{3}\Delta$  state: 4.7 ms for v = 0 and less than 1 ms for  $v \ge 1$ , which may contribute to the beginning of our decay curves. The abundance of the  $A' {}^{1}\Sigma$  state, the lifetime of which is expected to be very long, is too small ( $\le 4\%$ ) to contribute

TABLE I. Relative population of the NO<sup>+</sup> electronic states formed by electron impact ionization: present evaluation compared to literature values.

		O'keefe	Wilcox		
	Present	Ref. 8	Ref. 5		
$\overline{X^{1}\Sigma^{+}}$	11	15	50		
$a^{3}\Sigma^{+}$	5.3	7	3.2		
<i>b</i> <sup>3</sup> Π	34	36	18		
$W^{3}\Delta$	18.6		11		
		24			
b' <sup>3</sup> Σ -	8.7		4.6		
$A'^{1}\Sigma^{-}$	3.6	< 5	1.8		
$W^{1}\Delta$	3.7	> 5	3.5		
<i>Α</i> 'Π	14.4	18	7.6		

significantly to the observed signal. Therefore, 5 ms after ionization most of the singlet states are relaxed to the ground  $X^{1}\Sigma^{+}$  state and the triplets to the lowest  $a^{3}\Sigma^{+}$  state. Since two different sets of values are proposed in the literature for the relative population of the NO<sup>+</sup> electronic states<sup>5,8</sup> the initial populations have been reevaluated using the photoelectron spectra intensities<sup>17,18</sup> and calculated Franck–Condon factors.<sup>19</sup> As shown on Table I, values close to Ref. 8 have been obtained: 66% of the ions are in the triplet states instead of 37% according to Ref. 5.

The vibrational population of NO  $^+$  ( $a^3\Sigma^+$ ) after radiative decay of the upper states has been evaluated using Franck–Condon factors based on the potential curves of Albritton *et al.*<sup>19</sup> As shown in Table II, there is a very broad distribution: levels up to v = 4 are significantly populated. The absolute values may not be accurate since photoionization and electron impact may give different populations. However, since there is no available data on electron impact ionization cross sections for the various electronic states involved, the optical approximation seems reasonable for 70 eV electrons. Anyway this evaluation clearly shows that more than one vibrational level of NO  $^+$  ( $a^3\Sigma^+$ ) is populated, and this is confirmed by the reactivity with Ar and the difference of the lifetimes determined with Ar and CO<sub>2</sub> as monitors.

Modification of this distribution prior to reaction depends on the experimental conditions. In flowing afterglow<sup>2,3</sup> it was concluded from the very low reaction rate with Ar  $(5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ compared to } 7.2 \times 10^{-10} \text{ for the collision rate})$  that all the levels higher than v = 0 were quenched by the time the ions reached the reaction region. In contrast, in our experiments at least part of the v > 1 must be populated since the reaction with Ar is quite efficient (see below). An upper limit of the collision rate:  $7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  close to the rate  $(8 \pm 4 \times 10^{-10}) \text{ cm}^3 \text{ s}^{-1}$  measured

TABLE II. Vibrational population of NO<sup>+</sup> (a  ${}^{3}\Sigma^{+}$ ) after radiative decay of the upper states calculated using Franck–Condon factors based on the potential curves of Albritton *et al.* (Fig. 1).

v	0	1	2	3	4	5	6	7	8	9
Pop. %	12.4	12.2	11.0	8.6	5.9	4.1	3.0	2.2	1.5	1.0

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by Dotan et al.3 for

NO<sup>+</sup> 
$$(a^{3}\Sigma^{+}, v=0)$$
 + NO  $\rightarrow$  NO<sup>+</sup>  $(X)$  + NO.

With a typical pressure of  $6 \times 10^{-7}$  Torr and 0.5 ms residence time in the source, the quenching is less than 1%. So the vibrational population of the ions entering the relaxation cell must be close to the calculated values (Table II).

# **B. Reactivity**

Two different monitors have been used: Ar whose ionization potential lies between v = 0 and v = 1 of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ), and CO<sub>2</sub> which is 1.87 eV below v = 0 (Fig. 1).

### 1. NO<sup>+</sup>( $a^{3}\Sigma^{+}$ , v > 1)+Ar $\rightarrow$ Ar<sup>+</sup>+NO

It has been shown in flowing afterglow experiments<sup>2,3</sup> that the reaction rate constant with NO<sup>+</sup> ( $a^{3}\Sigma^{+}, v = 0$ ) is very small:  $3-5 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, the reaction being endothermic by 0.19 eV for v = 0.

In the present experiment, since the initial vibrational population is not relaxed in the ion source, the overall rate constant with argon is expected to be significantly larger. This rate constant has been determined in the following way:

The NO<sup>+</sup> ions are produced by a continuous electron beam, the other experimental conditions being the same as in the lifetime measurements. The ions are drifted through the central cell as quickly as possible in order to minimize radiative and collisional quenching. They reach the third cell in about 2 ms and react with argon. After a constant reaction time the product Ar<sup>+</sup> and remaining NO<sup>+</sup> are detected in the reaction cell with a picoammeter. The ratio  $[Ar^+]/([Ar^+] + [NO^+])$  is plotted as a function of Ar pressure (Fig. 2).

Integration of the kinetic equations for reaction and radiation gives

$$[\mathrm{Ar}^+] = \frac{[\mathrm{Ar}][\mathrm{NO}^{+*}]_0}{\{(1/\tau) + k \,[\mathrm{Ar}]\}} \times (1 - e^{-\{(1/\tau) + k \,[\mathrm{Ar}]\} \times t}),$$

where  $[NO^{+*}]_0$  is the concentration of NO<sup>+</sup>  $(a^{3}\Sigma^{+}, v \ge 1)$ entering the reaction cell,  $\tau$  the overall radiative decay to



FIG. 2. Plot of normalized argon signal as a function of Ar pressure used to determine k, the rate constant for the reaction NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ , v = 1) with Ar. The limit at high pressure gives the fraction of NO<sup>+</sup> in the ( $a^{3}\Sigma^{+}$ , v > 1) states.

states below v = 1, and k the overall rate constant of the NO<sup>+\*</sup>. Then

$$\frac{[Ar^{+}]}{[Ar^{+}] + [NO^{+}]} = \frac{[Ar^{+}]}{\Sigma[NO^{+*}]_{0}}$$
$$= \frac{k [Ar][NO^{+*}]_{0}}{\Sigma[NO^{+}]_{0} \times \{(1/\tau) + k [Ar]\}} \times (1 - e^{-\{(1/\tau) + k [Ar]\} \times t}).$$

The limit at high pressure is simply  $[NO^{+*}]_0 / \Sigma [NO^{+}]$ , the fraction of NO<sup>+</sup> in the  $(a^{3}\Sigma^{+}, v \ge 1)$  states reacting with Ar. The measured values:  $(20 \pm 2)\%$  is smaller than the calculated one ~50% (see Table II). This may be due to collisional relaxation in the reaction cell and (or) to reduced reactivity of the upper vibrational levels.

The rate constant given by

$$\frac{[\mathrm{Ar}^+]_{\infty} - [\mathrm{Ar}^+]}{\Sigma[\mathrm{NO}^+]_0} = e^{-\{(1/\tau) + k[\mathrm{Ar}]\} \times t}$$

is  $k = (6.5 \pm 1.5) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> close to  $k_{coll} = 7.2 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>.

The vibrational state dependence of the reaction cross section of NO<sup>+</sup> with Ar has been studied with state selected NO<sup>+</sup> ions in a TESICO experiment.<sup>6</sup> At the lowest collision energy (1.4 eV cm) the reaction cross section was found to be maximum at v = 2 and around four times smaller for v = 0,1 and two times smaller for v = 3-5.

This dependence is expected to be different at thermal collision energy. For v = 0 the reaction cross section should become very small, since endothermicity is not compensated by kinetic energy. On the other hand, the maximum at v = 2 predicted for a quasiresonant charge transfer occurring at large internuclear distances, will probably be smoothed out at thermal energy. Therefore, an upper limit of the overall reaction rate is obtained if all significantly populated levels except v = 0 are supposed to react at the same rate.

### 2. $NO^+(a^3\Sigma^+, v \ge 0) + CO_2 \rightarrow CO_2^+ + NO$

The reaction rate constant of NO<sup>+</sup> ( $a^{3}\Sigma^{+}, v$ ) with CO<sub>2</sub> determined in the same way as with Ar (see above) is  $k = 1.1 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> in good agreement with the literature values.<sup>2,3,8</sup> This is not surprising since the reaction being already exothermic for v = 0, its rate constant should not be sensitive to the vibrational states distribution. The fraction of NO<sup>+</sup> in the ( $a^{3}\Sigma^{+}, v \ge 0$ ) states is ( $33 \pm 2$ )%, also smaller than the calculated value (62%). Population of the v = 0 level deduced from these experiments: (33-20) = 13%, is very close to the calculated value: 12.4%.

#### C. Lifetimes

A typical decay curve with argon as monitor gas is shown on Fig. 3(a). Using various monitor gas pressures  $(1.2-2\ 10^{-5}\ \text{Torr})$  and electron energies (40 and 60 eV), the mean value obtained for the apparent lifetime is: 75  $\pm$  15 ms.

Since there is no information on the reactivity and lifetimes of the different vibrational levels, only correction of the apparent lifetime for quenching in the relaxation cell can be evaluated.



FIG. 3. Typical decay curves of normalized monitor ion intensity as a function of relaxation time using argon as monitor gas for v>1 (a), using CO<sub>2</sub> as monitor gas for v>0 (b). The slopes of the best fit lines yield lifetimes of 75 and 100 ms, respectively, which must be corrected for reactions in the relaxation cell. The corrected values obtained are 100 ms with Ar and 135 ms with CO<sub>2</sub> (see the text).

In addition to the background pressure in the relaxation cell ( $\sim 5 \times 10^{-8}$  Torr, mainly H<sub>2</sub>O), there was  $\sim 0.4 \times 10^{-8}$  Torr of NO leaking from the source and  $10^{-7}$ Torr of Ar leaking from the reaction cell. An upper limit of the correction is obtained on assuming the same rate constant (collision rate) for all the vibrational levels  $v \ge 1$ , i.e.,  $7.5 \times 10^{-10}$ ,  $1.4 \times 10^{-9}$ , and  $7.2 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> with NO, H<sub>2</sub>O, and Ar, respectively.

The lifetime thus corrected for collisional quenching in the relaxation cell is:  $100 \pm 20$  ms. This is an overall lifetime corresponding to the radiative relaxation of all the NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ,  $v \ge 1$ ) either to the (v - 1) level of the same electronic state or to the ground state (or a combination of them).

The apparent radiative decay obtained with CO<sub>2</sub> as monitor is  $100 \pm 20$  ms [Fig. 3(b)]. An upper limit of the quenching in the relaxation cell has been calculated with  $5 \times 10^{-8}$  Torr of H<sub>2</sub>O,  $0.4 \times 10^{-8}$  Torr of NO and  $5 \times 10^{-8}$ Torr of CO<sub>2</sub>. Correction of the apparent lifetime for collisional quenching in the relaxation cell gives  $\tau_{rad} = (135 \pm 25)$  ms. This is the overall radiation decay rate of all the NO<sup>+</sup> ( $a^{3}\Sigma^{+}, v$ ) states including v = 0 down to NO<sup>+</sup> ( $X^{1}\Sigma^{+}$ ).



FIG. 4. Normalized monitor ion intensity as a function of relaxation time. The least squares fit of the curve gives an apparent lifetime of 25 ms which must be corrected for reactions in the relaxation cell. Repeat measurements gave a corrected value of  $30 \pm 6$  ms.

The difference with the value obtained with Ar as monitor gas is significant.

# IV. $O_2^+(a \ ^4\Pi_u)$

### A. Population of the excited state

The  $O_2^+$  ions were produced by ionization of  $2-3 \times 10^{-7}$ Torr of  $O_2$  with 80 eV electrons. The fraction of metastable  $O_2^+$  entering the relaxation cell (which depends on the experimental conditions) was about 50% (see Sec. IV B). As discussed by O'Keefe and Mc Donald,<sup>8</sup> a broad distribution of the  $a \, {}^4\Pi_u$  vibrational population is expected from the initial FC population of the *a* and *b* quartet states followed by  $b \rightarrow a$  radiation ( $\tau = 1 \, \mu$ s). Anyway, as there is no monitor reaction available above the  $O_2^+$  ( $a \, {}^4\Pi_u$ , v = 0) state, the measured lifetime is a mean value corresponding to radiation of all populated levels of the excited state down to the ground electronic state.

### B. The monitor reaction: $O_2^+(a \, {}^4\Pi_u, v) + Ar \rightarrow Ar^+ + O_2$

Ar was chosen, instead of CO<sub>2</sub> used by Kuo *et al.*,<sup>9</sup> because its ionization potential is much closer to the energy of O<sub>2</sub><sup>+</sup> ( $a^{4}\Pi_{u}, v = 0$ ): 0.08 eV for Ar<sup>+</sup> ( $P_{1/2}$ ) and 0.26 eV for Ar<sup>+</sup> ( $P_{3/2}$ ), while CO<sub>2</sub><sup>+</sup> lies 2.24 eV below, close to v = 8 of the ground electronic state.

The rate constant of the monitor reaction, determined in the same way (see Sec. III B 1) as for NO<sup>+</sup>  $(a^{3}\Sigma^{+}, v \ge 1)$ is:  $k = (4.4 \pm 1) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. It is in good agreement with the literature values:  $(5 \pm 2) \times 10^{-10}$ ;<sup>1</sup>  $(4 \pm 1) \times 10^{-10}$ ;<sup>2</sup>  $(4.9 \pm 1.5) 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup><sup>8</sup> and somewhat smaller than the capture rate constant,  $7.1 \times 10^{-10}$ cm<sup>3</sup> s<sup>-1</sup>. The limit at high pressure, which is the fraction of O<sub>2</sub><sup>+</sup>  $(a^{4}\Pi_{\mu})$  reacting with Ar is 50%.

#### C. Radiative lifetime

The apparent lifetime determined from decay curves such as shown on Fig. 4 is:  $\tau_{app} = (25 \pm 5)$  ms. Correction for reaction in the relaxation cell with Ar leaking from the third cell  $(1 \times 10^{-7} \text{ Torr})$  and the background H<sub>2</sub>O  $(\sim 5 \times 10^{-8} \text{ Torr})$  gives an overall radiative lifetime  $\tau_r = (30 \pm 6) \text{ ms.}$ 

### **V. DISCUSSION**

# A. NO+(a <sup>3</sup>Σ+)

The experimental lifetimes of the present study are much shorter than the previously reported values and the differences are far off the estimated experimental uncertainties.

The large discrepancy with O'Keefe and Mc Donald<sup>8</sup> is not surprising since they used a single section ICR cell containing a mixture of NO and of the monitor gas  $CO_2$  to produce the ions, to let them relax and react, and to detect them. As a consequence the total pressure had to be kept very low:  $2-9 \times 10^{-8}$  Torr of CO<sub>2</sub> with only 1% of NO (close to the base pressure) and the lifetimes were obtained rather indirectly by extrapolating at zero CO<sub>2</sub> pressure the appearance rate of the monitor ion CO<sub>2</sub><sup>+</sup>.

The difference with Kuo *et al.*,<sup>9</sup> is more puzzling since in their experiments the production, radiative relaxation, and monitor reaction processes were separated in time by introducing NO and CO<sub>2</sub> successively through pulsed valves, so that the lifetime could be determined directly from the amount of CO<sub>2</sub><sup>+</sup> as a function of NO<sup>+</sup> relaxation time (i.e., delay between the two gas pulses). However the same experimental problems<sup>20</sup> which affected the NO<sup>+</sup> (X,v) lifetime measurements<sup>21</sup> may also have distorted the measured lifetime of the metastable ions.

Another likely explanation for the difference in the measured lifetimes is the fact that several vibrational and rotational levels of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) are populated and have no reason to decay at the same rate. Therefore, the experimental decay curves are in fact multiexponential and their shape depends as well on the radiative lifetimes as on the relative population of the vibrational and rotational states involved. The vibrational populations are probably similar in the two experiments although collisional deactivation during the ionization step is somewhat larger in the pulsed valve experiment since the number of collisions experienced by the ions is at least four times larger. In contrast, the rotational populations are obviously different: (near)thermal distribution in our ion source, preferential population of low J in the pulsed beam. J and hyperfine structure dependence of the lifetime has not been established for NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ). However, a strong dependence has been predicted in a recent theoretical paper "... for all the long lived NO+ triplet states capable of borrowing oscillator strength from the  $A^{-1}\Pi$ 

Another important difference between the two experiments is the observation time window: 10–150 ms in our case, compared to 60–500 ms in Ref. 9 As a consequence the two experiments clearly probe different parts of the multiexponential curve, i.e., of the lifetimes distribution: short lifetimes in the present experiment, longer in Ref. 9, and even longer in Ref. 8 where the observation window was 100 to 1500 ms.

An estimate of the radiative lifetime of v = 0 has been calculated on the basis of an approximate perturbation model. In this model the transition  $a^{3}\Sigma^{+} \rightarrow X^{1}\Sigma^{+}$  is considered to occur by mixing the triplet state with the closest (in energy) singlet state, i.e.,  $A^{1}\Pi$ .

The decay rate of the  $a^{3}\Sigma^{+}(v)$  state is

$$1/\tau = (64\pi^4 v^3/3 hc^3) \langle a^3 \Sigma^+ | er | X^1 \Sigma^+ \rangle^2,$$

where v is the  ${}^{3}\Sigma^{+}(v) \rightarrow {}^{1}\Sigma^{+}(v'')$  vertical transition wave number and  $\langle a {}^{3}\Sigma^{+}|er|X^{1}\Sigma^{+}\rangle$  the corresponding electronic transition dipole moment  $\mu_{a} {}^{3}\Sigma^{+}(v)$  This dipole moment is given by<sup>22</sup>

$$\mu_{a^{3}\Sigma^{+}(v)}^{2} = \sum_{v} \frac{\langle A^{1}\Pi | H_{so} | a^{3}\Sigma^{+} \rangle^{2}}{\left[ E \left[ a^{3}\Sigma^{+}(v) \right] - E \left[ A^{1}\Pi(v') \right] \right]^{2}} \\ \times \langle v | v' \rangle^{2} \mu_{A^{1}\Pi(v')}^{2}.$$

Since the lifetime of the  $A^{1}\Pi$  state is  $(1/\tau') = (64\pi^{4}\nu'^{3}/3 hc^{3})\mu_{A^{1}\Pi(v')}^{2}$ , where  $\nu'$  is the  ${}^{1}\Pi(v') \rightarrow {}^{1}\Sigma(v'')$  vertical transition wave number, it comes out

$$\frac{1}{\tau} = \sum_{v'} \frac{\langle A^{1}\Pi | H_{so} | a^{3}\Sigma^{+} \rangle^{2} \langle v | v' \rangle^{2}}{\left[ E \left[ a^{3}\Sigma^{+} (v) \right] - E \left[ A^{1}\Pi (v') \right] \right]^{2}} \\ \times \left( \frac{\nu}{\nu'} \right)^{3} \frac{1}{\tau'}.$$

The following data have been used to calculate  $1/\tau$ : a spinorbit coupling operator  $H_{so} = 19 \text{ cm}^{-1} 2^3$  independent of v', Franck-Condon factors calculated by Lefebvre-Brion, energies (wave numbers) taken from the tables provided by Albritton *et al.* and  $\tau' = 56$  ns also independent of v'. This gives a lifetime of 400 ms for v = 0.

The main problem in this calculation is certainly the magnitude of the spin-orbit coupling which has been estimated from the measured perturbation of the  $A^{1}\Pi$  state by another triplet state  $b'^{3}\Sigma^{-22}$  An error of 50% on this estimate would change the calculated lifetime by more than a factor of 2.

There is an obvious need for reliable calculations of the  ${}^{3}\Sigma^{+} \rightarrow {}^{1}\Sigma^{+}$  transition moments as well as of the transition moments within the  ${}^{3}\Sigma^{+}$  state. According to recent calculations<sup>24</sup> the vibrational transitions are much slower than in ground state NO<sup>+</sup>.<sup>25</sup> Lifetimes ranging from 450 to 109 ms have been found for v = 1 to 5, indicating that vibrational and electronic transitions both contribute to the overall lifetimes and in particular to the difference between the lifetimes measured using CO<sub>2</sub> and Ar as monitors.

# B. $O_{2}^{+}(a \, {}^{4}\Pi_{u})$

Like in the case of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ , v), the present experimental value is shorter than the two other values obtained with the monitor ion technique.<sup>8,9</sup> It lies in between the two lifetimes obtained by photodissociation and assigned to the  $F_1$ ,  $F_4$  and  $F_2$ ,  $F_3$  spin components.<sup>7</sup>

The possible influence of the experimental procedure on the measured lifetimes has been discussed for NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) (see above). The same remarks hold for O<sub>2</sub><sup>+</sup> ( $a^{4}\Pi_{u}$ ). Moreover using CO<sub>2</sub> as monitor<sup>9</sup> may introduce another problem: CO<sub>2</sub> may react with high vibrational levels ( $v \ge 8$ ) of the ground electronic state which are populated at least up to v = 10 by radiation from the  $A^2 \Pi_u$  state and also, for long relaxation times, from the  $a^4 \Pi_u$  state.

Reaction of  $CO_2$  with these nonradiating states would artificially increase the measured lifetime.

The lifetime dependence on the rotational and spin states (J and F), has been discussed in detail<sup>9</sup> using a first order perturbation model similar to the model we used for NO<sup>+</sup>. The excellent agreement found between theory and experiment was considered as "surprising"<sup>9</sup> since the model implies many approximations. Besides, it would be surprising that the relaxation time should not depend on the vibrational state at least through the spin-orbit coupling and the energy difference between the  $a \, {}^{4}\Pi_{u}$  vibrational levels and the  $A \, {}^{2}\Pi_{u}$  perturbing state. The only point which seems to be clearly established is the existence, for each vibrational level, of a whole set of radiative lifetimes: short for high J and all spin states, long for low J and  $F_{1}$ ,  $F_{4}$  spin states. In this case like in NO<sup>+</sup> ( $a \, {}^{3}\Sigma^{+}$ ) a broad lifetime distribution cannot be discarded.

### **VI. CONCLUSION**

The radiative lifetimes of metastable NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ) and O<sub>2</sub><sup>+</sup> ( $a^{4}\Pi_{u}$ ) have been remeasured using the monitor ion technique in a triple cell FT-ICR spectrometer.

For NO<sup>+</sup> the overall lifetime of  $v \ge 0$  has been determined using CO<sub>2</sub> as monitor, like in the previous FT-ICR experiments<sup>8,9</sup> and also the lifetime of  $v \ge 1$  using Ar as monitor. For O<sub>2</sub><sup>+</sup> only the lifetime of  $v \ge 0$  could be determined using Ar as monitor instead of CO<sub>2</sub> which can also react with high vibrational levels of the ground state.

In both cases the present values are significantly smaller than those obtained by the same technique but in rather different experimental conditions. As discussed above, part of the difference between the experimental results may be due to experimental artifacts. But most of it can be explained by the population of several vibrational and rotational states decaying at different rates. The resulting multiexponential decay may be approximated, within the experimental uncertainties, to a single exponential but, of course, the corresponding overall lifetime depends on the observation time window which is different in the three experiments.

In contrast with vibrational transitions in ground electronic states or spin allowed electronic transitions, there is no published *ab initio* calculation on the transition moments of metastable ions. Therefore, only an approximate perturbation model, including some very questionable approximations, has been used so far and any quantitative conclusion seems hazardous. Fortunately, two theoretical groups got interested in this problem and new calculations are in progress for NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ ,v) both for the vibrational transitions within the electronic state<sup>24</sup> and for the electronic transition  $a^{3}\Sigma^{+} \rightarrow X^{1}\Sigma^{+}$ .<sup>26</sup>

### ACKNOWLEDGMENTS

We gratefully acknowledge the support of CNRS, and of the Air Force Office of Scientific Research under Grant No. AFOSR 87-0390. We greatly appreciated our discussions with G. Chambaud, H. Lefebvre-Brion, P. Rosmus, and D. Yarkony, and we would like to thank particularly H. Lefebvre-Brion for calculating the Franck–Condon factors needed to evaluate the NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ , v = 0) lifetime, and G. Chambaud and P. Rosmus for communicating their results on the vibrational decay rates of NO<sup>+</sup> ( $a^{3}\Sigma^{+}$ , v) prior to publication.

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