

## EXPERIMENTAL MEASUREMENT OF THE RADIATIVE LIFETIME OF $\text{NO}^+(\text{X}^1\Sigma^+, \nu=1, 2 \text{ AND } 3)$

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The radiative lifetimes of  $\text{NO}^+(\text{X}^1\Sigma^+, \nu=1, 2 \text{ and } 3)$  have been measured in a new Fourier transform ion cyclotron resonance (FT/ICR) apparatus using the monitor ion technique. Resonance-enhanced multiphoton ionization (REMPI) via the  $\text{C}^2\Pi$  Rydberg state of NO was used to prepare vibrationally state-selected  $\text{NO}^+(\text{X}, \nu)$ . Photoelectron spectroscopy experiments indicate  $\nu=2$  was formed with greater than 97% purity and  $\nu=3$  with greater than 91% purity, consistent with literature values of Miller and Compton which indicate good vibrational selection for  $\nu=0$  and  $\nu=1$ . The radiative lifetimes of the  $\text{NO}^+(\text{X}) \nu=1, 2$  and 3 vibrational states were measured to be 90, 32 and 16 ms, respectively. Comparison is made with theory and other experiments where available.

### 1. Introduction

The natural radiative lifetime of a quantum state is one of its most important properties, affecting such diverse fields as plasma chemistry, energy transfer and storage, relaxation phenomena in ionized and shocked atmospheres, state-selected chemistry, and basic chemical synthesis in interstellar clouds. Consequently substantial effort, both experimental and theoretical, has gone into developing methods for obtaining radiative lifetimes [1].

For stable, simple, neutral molecules the procedure usually entails either measurement of time-resolved fluorescence (electronic states with  $10^{-6}$  to  $10^{-9}$  s lifetimes) or absolute absorption cross sections (usually vibrational states with  $10^{-3}$  to 1 s lifetimes). For many of the most interesting systems, however, such measurements are extremely difficult or impossible to make. These include most radicals and ions as well as other unusual or high energy species. The reasons for this are simple; these systems cannot be easily prepared in abundance and are usu-

ally extremely reactive and thus cannot be simply accumulated or stored. Yet these species are precisely those that are most often involved in important processes such as the chemistry in laser cavities [2], the interstellar medium [3], and chemical energy storage.

The theoretical Einstein  $A$  coefficients (i.e. the radiative lifetimes) for the lowest lying vibrational states of the ground electronic state of  $\text{NO}^+$  have been calculated by Werner and Rosmus [4] and Billingsley [5]. The absorption technique has been used by Bien [6] and the chemical reaction or "monitor ion" technique by Hening et al. [7] in measuring these coefficients. In this paper we describe a new technique for measuring radiative lifetimes for simple ions and apply it to the  $\text{NO}^+(\text{X}, \nu)$  system. Comparisons will be made with theory and experiment where possible.

### 2. Experimental

A detailed account of the principles of the FT/ICR technique can be found elsewhere [8]. The details of

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the specific ICR spectrometer used in our studies are given elsewhere [9]. Only a brief summary is given here. A simplified schematic of the main vacuum chamber of our apparatus is shown in fig. 1. The top-most section is equipped with two Newport pulsed valves and is pumped by a 550  $\ell/s$  turbomolecular pump. The valves were equipped with a 0.5 mm diameter nozzle and typical NO backing pressures were approximately 1 atm. The lower, main chamber is pumped by a 1500  $\ell/s$  turbomolecular pump. The chambers are connected by two skimmers, each with a 1.3 mm diameter hole. Under typical conditions, with one pulsed valve operating, pressure in the pulsed valve chamber is maintained at  $6 \times 10^{-6}$  Torr or less to minimize collisions between the molecular beam and background gas before the molecular beam goes through the skimmer. The pressure in the main chamber is maintained at a background pressure of  $2 \times 10^{-8}$  Torr or less for better detection efficiency with the FT detection technique, and to minimize collisional deactivation of the state-selected ions in the ICR cell. An IonSpec electronics console is used for the FT detection. An electromagnet is used at 0.4 T. The direction of the magnetic field is perpendicular to the nozzle beam and the laser beam directions.

Resonance-enhanced multiphoton ionization is used to create vibrationally state-selected  $\text{NO}^+$  ions. High purity of these states is essential. Photoelectron spectra of  $\text{NO}^+(X, v)$  for  $v=0$  and 1, produced via 2+1 REMPI through the  $C^2\Pi$  state of NO, have been obtained by Miller and Compton [10]. Their study indicates that this technique produces  $\text{NO}^+(X)$  in

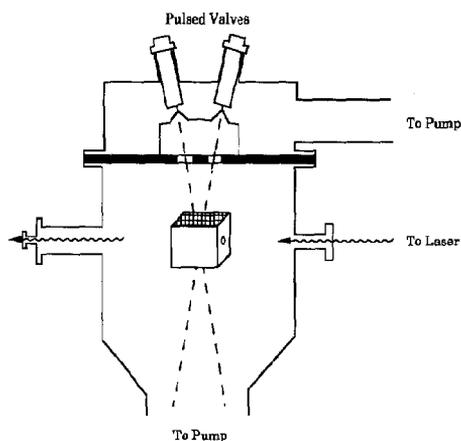


Fig. 1. Schematic of the FT/ICR spectrometer vacuum chamber.

the  $v=0$  and  $v=1$  states with greater than 90% purity. We have investigated the  $v=2$  and  $v=3$  states using a similar method. Our study was performed using the time-of-flight photoelectron energy analyzer described by Allendorf et al. [11]. The angle-integrated vibrational branching ratios measured indicate that 2+1 REMPI through the  $\text{NO}(C, v)$  states produces  $\text{NO}^+(X, v=2)$  with greater than 97% purity and  $\text{NO}^+(X, v=3)$  with greater than 91% purity (see fig. 2). Hence, as compared to electron impact methods which create a wide range of internal energies, multiphoton ionization is the technique of choice for production of state-selected  $\text{NO}^+(X, v)$ .

The NO molecules are cooled by expansion through the nozzle. Analysis of the excitation spectra for  $v=3$  of  $\text{NO}^+$  indicates the ions have a rotational temperature of about 20 K [9], with only the first few rotational levels populated.

The  $\text{NO}^+$  excited state population is monitored by

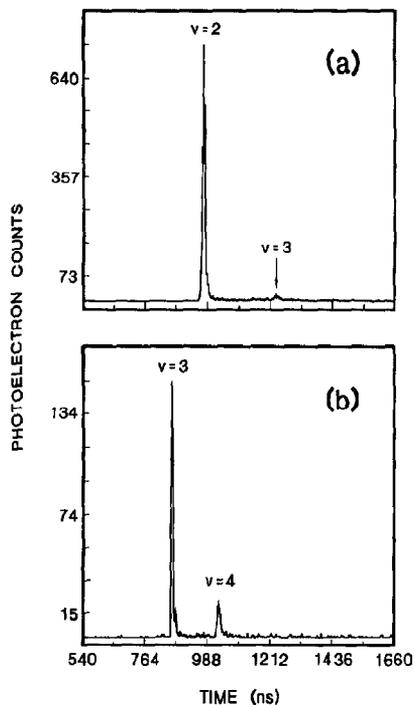
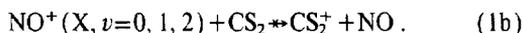


Fig. 2. 2+1 resonant multiphoton ionization photoelectron spectra for formation of  $\text{NO}^+(X^1\Sigma^+, v)$  via  $\text{NO}(C^2\Pi, v)$ . In (a) the  $v=2$  state of  $\text{NO}(C)$  is accessed and in (b) the  $v=3$  state of  $\text{NO}(C)$  is accessed. The spectra shown are for a laser polarization of  $0^\circ$  with respect to the electron flight path to the detector. Angle averaging yields  $>97\%$   $v=2$  in (a) and  $>91\%$   $v=3$  in (b).

the charge transfer product from a neutral "monitor gas", chosen to react with  $\text{NO}^+(v)$  but not with  $\text{NO}^+(v-1)$ . For  $\text{NO}^+(v=3)$ , this monitor gas is  $\text{CS}_2$ . The pertinent reactions are



Reaction (1b) is endothermic and immeasurably slow for  $\text{NO}^+(X, v=0, 1, 2)$ . For  $v=2$  we see no  $\text{CS}_2^+$  product signal indicating a rate constant less than  $1 \times 10^{-11} \text{ cm}^3/\text{s}$ . Reaction (1a) is exothermic with a rate constant of  $\approx 1 \times 10^{-9} \text{ cm}^3/\text{s}$ . Details will be presented elsewhere [12].

The experimental pulse sequence for lifetime measurements is shown in fig. 3. After application of a quench pulse to remove unwanted ions from the cell, the first pulsed valve is fired and NO gas is injected into the IRC cell. This pulse has a well-defined beam width of  $100 \mu\text{s}$ , and is intercepted at the center of cell by a  $35 \text{ ns}$  long pulsed laser beam, forming the vibrationally state-selected ion of interest. Since the molecular beam is only about  $100 \mu\text{s}$  long [9], the loss of  $\text{NO}^+$  due to collisional deactivation is estimated to be less than 2%. This estimate assumes a

peak "pressure" in the NO beam of  $2 \times 10^{-5} \text{ Torr}$  and a deactivation rate constant of  $5 \times 10^{-10} \text{ cm}^3/\text{s}$  [12]. (The pressure estimate is made by comparing signal levels from the pulsed valve and from a continuous flow method of introducing NO gas into the ICR cell.) The second valve is pulsed after a variable delay time to allow  $\text{NO}^+(X, v)$  variable relaxation time before reacting with the monitor gas, in this case  $\text{CS}_2$ . This second valve is open for a substantially longer time than the first to increase the  $\text{CS}_2$  concentration in the ICR cell and thus enhance the  $\text{CS}_2^+$  monitor ion signal. A reaction time of  $35 \text{ ms}$  is achieved by applying the detect pulse  $35 \text{ ms}$  after the second pulsed valve is fired. This reaction time was chosen based upon typical operating pressures and the rate of reaction of  $\text{CS}_2$  with  $\text{NO}^+(X, v=3)$ .

The  $\text{CS}_2^+$  appearance signal is described by [9]

$$[\text{CS}_2^+]_t = A[\text{NO}^+(v=3)]_{t=0} \exp(-t_d/\tau_v), \quad (2)$$

where  $t_d$  is the delay time between the laser and the second pulsed valve and  $\tau_v$  the radiative lifetime of the ion state of interest. The scaling constant  $A$  depends on the  $\text{CS}_2$  pressure during the  $35 \text{ ms}$  reaction time as well as the  $\text{CS}_2/\text{NO}^+(v=3)$  reaction rate. Rearrangement of (2) yields

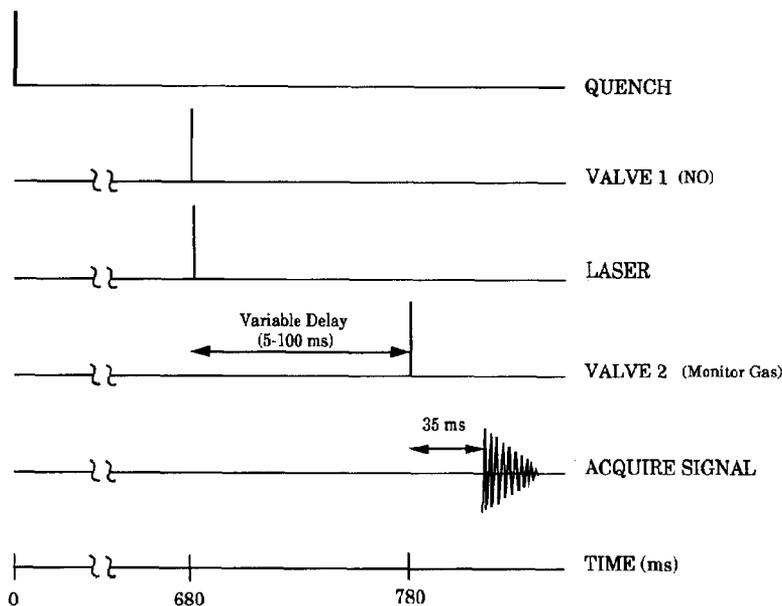


Fig. 3. The experimental pulse sequence used in the radiative lifetime measurements. The transient is not drawn to scale; typical acquisition width  $\approx 0.8 \text{ ms}$ .

$$\ln([CS_2^+]_t/[NO^+(v=3)]_{t=0}) = -t_d/\tau_v + \text{constant} . \quad (3)$$

The term  $[NO^+(v=3)]_{t=0}$  can be written

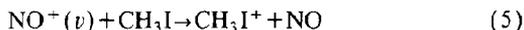
$$[NO^+(v=3)]_{t=0} = [NO^+(v=3)]_t + [NO^+(v=2, 1, 0)]_t + [CS_2^+]_t .$$

Since the FT detection system cannot distinguish between  $NO^+(v)$  and  $NO^+(v')$ , the detected  $NO^+$  signal is actually the sum of these two terms. Hence,

$$\ln\left\{\frac{[CS_2^+]_t}{([NO^+]_t + [CS_2^+]_t)}\right\} = -t_d/\tau_v + \text{constant} . \quad (4)$$

A plot of the left-hand side of eq. (4) versus delay time yields a straight line of slope  $-1/\tau_v$ . The value of the constant may vary slightly from day to day depending on operating conditions; however, this will not affect the lifetime measurement since the slope does not change.

The monitor gas used for both  $v=1$  and  $v=2$  was  $CH_3I$ . This was possible because the charge transfer rate constant for the reaction



was two orders of magnitude faster for  $v=2$  than for  $v=1$ . This important and surprising result will be discussed further in a subsequent publication [13].

### 3. Results

Fig. 4 shows results for the lifetimes of the  $v=1$ , 2 and 3 states of  $NO^+(X)$ , displayed in the form of eq. (4). Contributions from higher-lying vibrational states can be ignored; in the worst case,  $NO^+$  state selection is greater than 91% pure, as indicated by the photoelectron studies. The slopes of the best fit lines indicate that the lifetimes of the  $NO^+(X)$   $v=1$ , 2 and 3 states are  $90 \pm 5$ ,  $31 \pm 2$  and  $16 \pm 1$  ms, respectively. Taking into account possible mass discrimination in the FT-ICR detector and possible collisional vibrational quenching from  $NO$  background gas, these uncertainties rise to  $90 \pm 10$ ,  $31 \pm 6$  and  $16 \pm 3$  ms. Each experiment was repeated a minimum

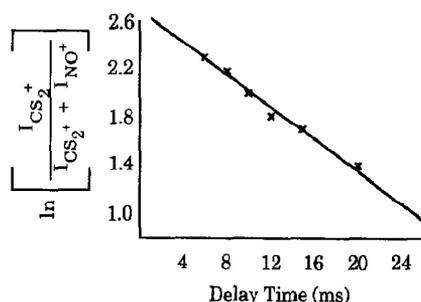
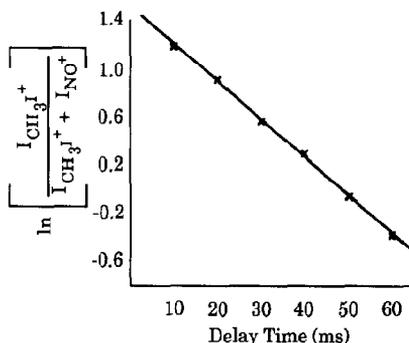
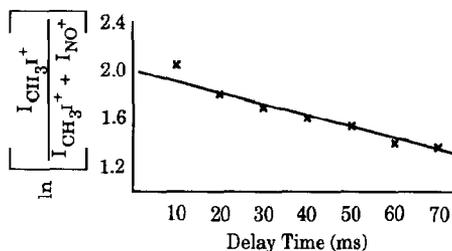


Fig. 4. Typical plots used to determine the radiative lifetime of  $NO^+(X, v)$ .  $v=1$  is shown in (a),  $v=2$  in (b), and  $v=3$  is shown in (c). The slope yields  $-1/\tau_v$ , where  $\tau_v$  is the radiative lifetime of the vibrational state of interest. In (a) and (b)  $CH_3I$  is the monitor gas while in (c)  $CS_2$  is the monitor gas.

of three times with the precision falling well within the error limits quoted.

#### 4. Discussion

The vibrational relaxation of  $\text{NO}^+(v \geq 1)$  in neutral collisions has been studied by Federer et al. [12] and Morris et al. [14]. The most effective background gas for collisionally quenching  $\text{NO}^+(v)$  is NO [12]. The maximum background pressure of NO in our system is less than  $2 \times 10^{-8}$  Torr, and it is probably substantially less than that. Under these conditions less than 2.3% of the state-selected  $\text{NO}^+(v)$  ions would undergo quenching collision with NO [12] (and substantially less for any other molecule [12]) at the *maximum* delay time. As mentioned, this effect has been accounted for in the uncertainty.

Table 1 compiles our experimental results along with those of Heninger et al. [7]. Also included are the lifetimes of  $\text{NO}^+(X, v=1, 2 \text{ and } 3)$  as calculated by Werner and Rosmus [4] and Billingsley [5]. Excellent agreement exists between both experimental results and the calculation of Werner and Rosmus for the  $v=1$  lifetime.

The agreement between experimental results for  $v=2$  is not quite as good, however. The likely explanation for the difference between our result and that of Heninger et al. lies in the difference in experimental techniques. To produce  $\text{NO}^+(v)$  ions, Heninger et al. use  $\approx 15$  eV electron impact on rotationally thermal NO. In our experiments,  $\text{NO}^+(v)$  is formed by multiphoton ionization on rotationally cool NO ( $\approx 20$  K). The wide range of vibrational states ( $v=0$  to 6) produced by electron impact contributes uncertainty to the source of Heninger's monitor ion signal. For example, Heninger et al. employ  $\text{CH}_3\text{I}$  and  $\text{NO}_2$  to monitor the  $\text{NO}^+ v=1$  and  $v=2$  populations, respectively. Both charge transfer

reactions are assumed to be fast, since both are exothermic. However, as previously discussed, our studies indicate that  $\text{NO}^+(v=1)$  reacts almost 100 times slower with  $\text{CH}_3\text{I}$  than does the  $v=2$  state. Further, reaction of  $\text{NO}_2$  with  $\text{NO}^+(v=2)$  is too slow to be detected with our apparatus ( $< 1 \times 10^{-11}$   $\text{cm}^3/\text{s}$ ) [13]. The added rotational energy in the electron impact generated  $\text{NO}^+(v)$  ions may contribute to the appearance of the monitor ion from a lower vibrational state than is seen in our experiment, although this seems unlikely. If these effects are considered, then the apparent lifetime of  $\text{NO}^+(v=2)$  obtained by Heninger et al. would be larger than our result, as is the case. It is also apparent that our lifetime for  $v=2$  is smaller than that predicted by theory. The discrepancy appears to be larger than the cumulative uncertainties in the two results. The discrepancy is even more apparent for  $v=3$ , as discussed next.

Our result for the  $v=3$  lifetime, 16 ms, is a factor of two smaller than the value predicted by the ab initio calculations of Werner and Rosmus. Our result is in somewhat better agreement with Billingsley, although his calculation is not as sophisticated as that of Werner and Rosmus. The difference in the two ab initio calculations comes mainly from the difference in the slopes of the calculated electric dipole moment functions, which depend heavily on the basis set chosen.

At this point it is not clear why our measurements are in disagreement with the calculation of Werner and Rosmus. Several checks were made on the experimental data. First, for  $\text{NO}^+(X, v=3)$  there is up to 9%  $\text{NO}^+(X, v=4)$  initially formed by the laser. Inclusion of 9%  $\text{NO}^+(X, v=4)$  into the analysis raises the lifetime we determine for  $\text{NO}^+(X, v=3)$  by 1 ms to 17 ms. In the analysis we assumed  $\tau_{v=4} = 0.5\tau_{v=3}$  and that the  $v=4$  ions react on every collision with  $\text{CS}_2$  to form  $\text{CS}_2^+$ .

We also obtained an estimate of  $\tau_{v=3}$  by using  $\text{CH}_3\text{I}$  as the monitor gas. The data are shown in fig. 5. In this case the analysis is complex. Both  $\text{NO}^+(X, v=2)$  and  $\text{NO}^+(X, v=3)$  react with  $\text{CH}_3\text{I}$  near the collision limit. From the knowledge of these rate constants and the radiative lifetime  $\tau_{v=2} = 31$  ms, we obtain a value  $\tau_{v=3} = 10 \pm 7$  ms. The rather large error arises from the uncertainties of the quantities needed to extract  $\tau_{v=3}$  from the kinetic analysis. While we do

Table 1  
Radiative lifetimes (ms) for  $\text{NO}^+(X^1\Sigma^+, v=1, 2, 3)$

v	Experiment		Theory	
	this work	ref. [7]	ref. [4] <sup>a)</sup>	ref. [5]
1	$90 \pm 10$	$95 \pm 15$	91	73
2	$31 \pm 2$	$46 \pm 10$	48	37
3	$16 \pm 3$	-	33	24 <sup>b)</sup>

<sup>a)</sup> Stated uncertainty in ab initio calculations  $\approx 20\%$ .

<sup>b)</sup> Calculated from the linear fit of Billingsley's electric dipole moment function.

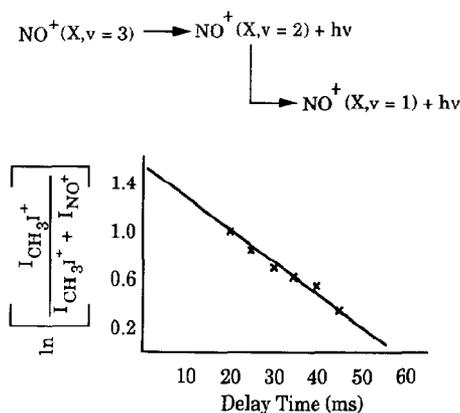


Fig. 5. Plot used to estimate the radiative lifetime of  $\text{NO}^+(X, v=3)$  using  $\text{CH}_3\text{I}$  as the monitor gas. A rather complex set of kinetics is needed to extract  $\tau_{v=3}$  from this graph (see text).

not consider this number accurate, it is certainly consistent with the more accurate value of  $\tau_{v=3} = 16_{-3}^{+3}$  ms reported in table 1.

The only potential source of significant error in our measurement is in detector discrimination. Accurate relative intensities of  $\text{NO}^+$  and the monitor ion ( $\text{CH}_3\text{I}^+$  or  $\text{CS}_2^+$ ) are needed to establish the abscissas in the plots used to obtain the radiative lifetimes (fig. 4). Known mixtures of these gases were introduced into the ICR cell and ionized by 70 eV electron impact. The resulting ratios measured were within 20% of those expected from the ionization cross sections of the gases. The tuning of the instrument in these calibration measurements was identical to that used when actual data was taken. In reporting the uncertainties of the measurements in table 1 we assumed possible discrimination of 100%, a full five times that which we measured. Even a discrimination of 1000% only raises the value of  $\tau_{v=3}$  to 25 ms. While we feel discrimination of 100% is on the outer reaches of possibility, a discrimination of 1000% is totally out of the question.

The experiment we do is so straightforward there are not many possible sources for error. The only absolute measurement made is of the vibrational populations formed in the REMPI experiment, and those results seem completely unambiguous. It appears that the discrepancy between experiment and theory is at present unexplained, and further work needs to be done to narrow the gap for this important system.

In summary, we have developed a technique to form vibrationally state-selected ions in an ICR ion trap in the absence of background gas. This method allows the study of such properties as radiative lifetimes and state-selected chemical reactivity. The current work demonstrates that with choice of a suitable monitor gas, the lifetimes of the  $v=1, 2$  and  $3$  states of  $\text{NO}^+(X)$  were determined to be 90, 31 and 16 ms, respectively. Work is currently in progress to locate suitable monitor gases for still higher vibrational states of  $\text{NO}^+(X)$ .

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