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DESY SR-77/23
December 1977

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Selected Fluorescence and Dissociation Lifetimes of N_2O^+ in its $\tilde{A}(^2\Sigma^+)$, 000 and 100 states.[+]

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[+] Work supported by Deutsche Forschungsgemeinschaft DFG and Deutsches Elektronensynchrotron DESY

Abstract:

Radiative and radiationless lifetimes together with the quantum yield towards fluorescence of individual vibronic states of molecular ions can be determined by threshold electron-fluorescence photon coincidence measurements. This method is here applied to the $\tilde{X}^2\Pi_{3/2,1/2}$ and $\tilde{A}\,^2\Sigma^+$ states of N_2O^+ which were also studied by high resolution photoionization resonance spectroscopy.

Introduction:

In previous publications /1/ spectroscopic results were presented for the linear triatomic ions CO_2^+, CS_2^+ and COS^+ by means of Photoionization resonance (PIR) spectroscopy /2/ a method which gives direct spectroscopic information about molecular ions. Interesting new effects in the vibronic structure of these ions could be observed - such as Renner-Teller effect or Fermi resonances. In addition the CO_2^+ ion was investigated in detail with respect to the fragmentation and to the radiative decay from selected vibronic states by threshold electron-ion and threshold electron-fluorescence photon (TEFP) coincidence measurements, respectively.

In particular, for the first time, TEFP coincidence measurements were employed to determine the radiative lifetimes by a measurement of the coincidence delay for individual selected vibrational levels of the $\tilde{A}$ and the $\tilde{B}$ state of CO_2^+ /1c/.

State selection and lifetime determination is achieved by filtering out the electrons with zero kinetic energy and by measuring the fluorescence photons in coincidence with these threshold electrons, since by these electrons intrinsically the state of the ion and the onset of the ionization is determined.

In the present work these measurements were applied to study the $\tilde{X}$ and the $\tilde{A}$ state of N_2O^+ with high resolution and especially the radiative and nonradiative decay of N_2O^+ in the (0,0,0) and (1,0,0) vibrational levels of the $\tilde{A}$ state. The interesting aspect is due to the fact that from the $\tilde{A}$ (0,0,0) state only fluorescence emission was observed although it lies well above two dissociation limits whereas from the $\tilde{A}$ (1,0,0) state fluorescence emission takes place in competition with dissociation /3,4/.

Experimental:

The experimental method and setup has been described previously /1/. Briefly, synchrotron radiation from the storage ring DORIS at DESY in Hamburg, West Germany is dispersed with a 3-meter scanning VUV monochromator (resolution 0.15 Å FWHM) and is used to photoionize the N_2O. The production of photoelectrons with zero kinetic energy as the photon energy (wavelength) is scanned yields the energy levels of individual molecular ions. For the lifetime measurements the threshold electrons from one particular vibronic state of the ion are detected in coincidence with the photons emitted from this state. One records then incident photon intensity, electrons, fluorescence photons and coincidences between the electrons and the fluorescence photons.

N_2O gas (99 % purity) was obtained from Linde AG and was used without further purification.

Spectroscopy:

The threshold electron spectra for the transitions

$$N_2O\ (\tilde{X}\,^1\Sigma^+) \longrightarrow N_2O^+(\tilde{X}\ ^2\Pi_{3/2,1/2}), \text{and} \longrightarrow N_2O^+\ (\tilde{A}\,^2\Sigma^+)$$

are shown in figures 1 and 2 respectively. The wavelengths obtained from these spectra are given in table 1. Table 2 contains vibrational frequencies and for the $\tilde{X}$ state, the spin-orbit separation. Comparison of the present data with other work /5,6/ is also made in table 2.

The ν_2 vibration of the $^2\Pi$ ground state of N_2O^+ is perturbed as expected by nuclear-electronic interactions - the Renner-Teller coupling. The location of the three most intense peaks due to the excitation of the bending vibration ν_2, namely the 010 $^2\Sigma^{(+)}$, the 010 $^2\Delta_{3/2}$ and the 020 $^2\Pi_{3/2,1/2}$ components at 957.9 Å, 956.4 Å and 954.2 Å, respectively, matches very well the values from fluorescence studies /5/; therefore taking into account these three peaks we obtain in a very direct way a Renner-Parameter ($\epsilon = 0.19$), which agrees with that from the fluorescence studies ($\epsilon = 0.1925$).

The large variation in intensity of the $\nu_2 = 1$ components which is similarly seen in the case of CO_2^+ /1a/, may in part result from the allowed nature of the $\Sigma^+ \rightarrow \Sigma^+$ transition as compared with the $\Sigma^+ \rightarrow \Sigma^-$ transition. Nevertheless, such a strong predominance is somewhat surprising from the fact that states with strong spin orbit interaction are generally presumed to have a poor retention of that +, - symmetry /7/. In addition, it is likely that autoionizing Rydberg states which are degenerate with the ionic state to which they decay contribute irregularly to the intensity of these transitions.

Fluorescence Measurements:

Using the threshold electron-fluorescence photon coincidence method for obtaining fluorescence lifetimes as recently developed in this laboratory /1c/, the lifetimes of the N_2O^+ $\tilde{A}$ $^2\Sigma^+$ (000) and (100) states were determined. The coincidence data are shown in figure 3 along with the lifetimes obtained. The raw data are given in table 3. A least squares fit of the data to the equation

$$n(t)\,dt = \left[A \cdot \exp\ (-t/\tau) + B\right] dt$$

was used, where A is proportional to the true coincidence counts B to the random coincidence counts and τ is the measured lifetime. This equation is appropriate for the present measurements where low count rates were encountered. These lifetimes, for which the initial (radiating) state is unambiguously determined, confirm the results of phase shift measurements on electron bombarded molecules /8,9,10/. From fragmentation studies on N_2O^+ ($\tilde{A}$) it was shown that the 000 state does not dissociate but that the 100 state does /4,12/. Using this information we can then say that the quantum yield for fluorescence from the N_2O^+ $\tilde{A}$ (000) state is unity. This in turn enables us to determine the quantum efficiency for fluorescence for the N_2O^+ $\tilde{A}$ (100) state (table 2). We obtain a value of $0 = 0.66$.

The directly measured lifetime of a particular state corresponds to the rate of depopulation observed via all possible exit channels taken together. For the 000 state, there is just the one channel and the measured lifetime corresponds to the radiative lifetime of this state. The non-unity quantum efficiency for the 100 state on the other hand indicates that at least one other exit channel exists, namely fragmentation. From the lifetime and quantum efficiency of the $\tilde{A}$ (100) state determined here, and using the relation $1/\tau_{obs} = 1/\tau_{Fluor} + 1/\tau_{Diss.}$, we obtain a radiative lifetime for this state of 250 ns and a dissociative lifetime of 490 ns. These results along with those obtained with other methods /4,8-11/ are summarized in table 4.

Acknowledgements:

Financial assistance for this research form the Deutsche Forschungsgemeinschaft and the Deutsche Elektronensynchrotron (DESY) are greatly appreciated. One of us (W.B. Peatman) is grateful for a NATO Travel Fellowship.

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Figure Captions:

1. Threshold Electron Spectrum showing the $\tilde{X}\ ^2\Pi$ state of N_2O^+.
2. Threshold Electron Spectrum showing the $\tilde{A}\ ^2\Sigma^+$ state of N_2O^+.
3. Threshold Electron-Fluorescence photon coincidence curves:
   (a) from the $\tilde{A}$ (0,0,0) state, (b) from the $\tilde{A}$ (100) state.

Table 1

Wavelengths derived from the PIR-spectra of N_2O

	Peak No.	(Å)	Energy(cm^{-1})	Designation
$\tilde{X}\ (^2\Pi_{3/2,1/2})$	0	963,3	103810	hot band
	1	961,7	103980	000 $\Pi_{3/2}$
	2	960,5	104110	000 $\Pi_{1/2}$
	3	957,9	104395	010 $\Sigma^{(+)}$
	4	956,4	104560	010 $\Delta_{3/2}$
	5	955,8	104620	010 $\Sigma^{(-)}$
	6	954,2	104800	020 $\Pi_{3/2,1/2}$
	7	951,5	105100	100
	8	950,3	105230	100
	9	947,7	105520	110
	10	945,9	105720	001
	11	944,8	105840	001
	12	941,7	106190	200
	13	940,4	106340	200
	14	937,9	106620	210
$\tilde{A}\ (^2\Sigma^+)$	1	756,4	132205	000
	2	748,7	133565	100
	3	742,5	134680	001
	4	741,2	134920	200
	5	735,2	136020	101
	6	734,0	136240	300

Table 2

Threshold electron data for N_2O^+ $\tilde{X}$ ($^2\Pi_{3/2,1/2}$) and $\tilde{A}$ ($^2\Sigma^+$)

Vibrational frequencies (cm^{-1}):

	Present work			Fluorescence Spectroscopy /5/			PES /6/	
	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_3
$\tilde{X}(^2\Pi_{3/2,1/2})$	1110 ± 15	420 ± 10*	1740 ± 15	1126,42	412,3*	1737,7	1140	1750
$\tilde{A}(^2\Sigma^+)$	1360 ± 15		2470 ± 15	1345,52	614,1	2451,7	1350	2460

Spin-orbit coupling constant (cm^{-1})

	Present work	Fluorescence Spectroscopy
$\tilde{X}(^2\Pi_{3/2,1/2})$	130	132,36

*(010), $\Sigma^{(+)}$ component ⟵ (000)

Table 3

Data from lifetime measurements on N_2O^+ $\tilde{A}$ ($^2\Sigma^+$)

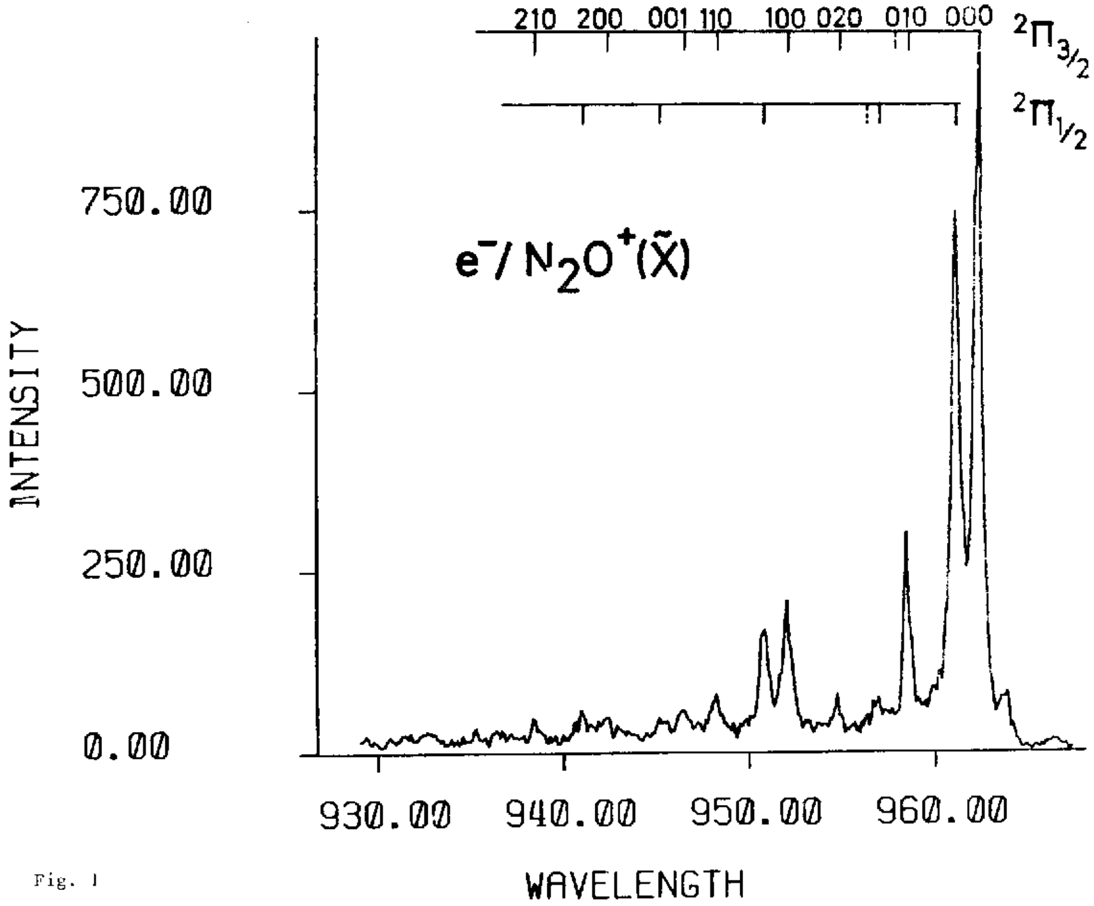
Vibrational State	Electrons (counts)	Coincidences (counts)	Quantum Efficiency	τ (nsec)
000	$8,586 \cdot 10^6$	8010	1*	220 ± 15
100	$9,354 \cdot 10^6$	5741	0,66	166 ± 15

* Taken as unity. See text.

Table 4

Lifetimes of the 000, 100 States of N_2O^+ $\tilde{A}$ ($^2\Sigma^+$)

	000	100		
	τ_{Fl} (nsec)	τ_{obs} (nsec)	τ_{Fl} (nsec)	τ_{Diss} (nsec)
Present work	220±15	166±15	250	490
Ref. 9 (Phase Fluor.)	232±20	188±20		
Ref. 10 (Phase Fluor.)	223±20	165±16		
Ref. 8 (Phase Fluor.)	260±20			
Ref. 11 (Coincidence)	240			
Ref. 4 (Coincidence)			275±60	410±90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$^2\Pi_{3/2}$
$^2\Pi_{1/2}$
$e^-/N_2O^+(\tilde{X})$
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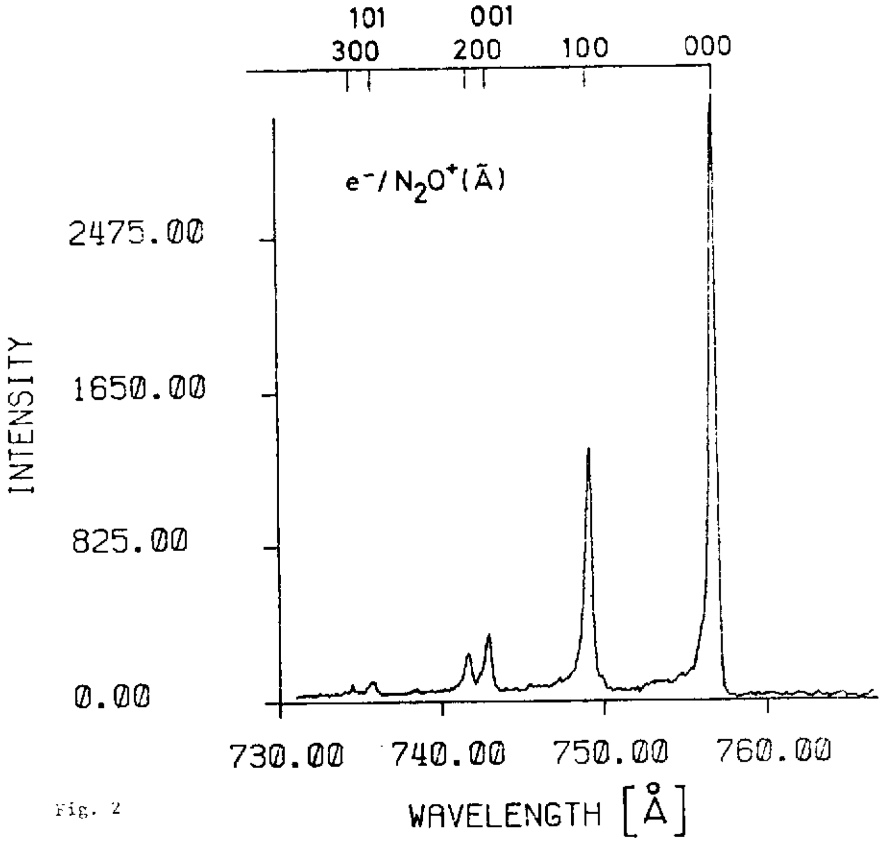
250.00
0.00
930.00
940.00
950.00
960.00
WAVELENGTH

Fig. 1


101
300
001
200
100
000
$e^-/N_2O^+(\tilde{A})$
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825.00
0.00
730.00
740.00
750.00
760.00
WAVELENGTH [Å]

Fig. 2

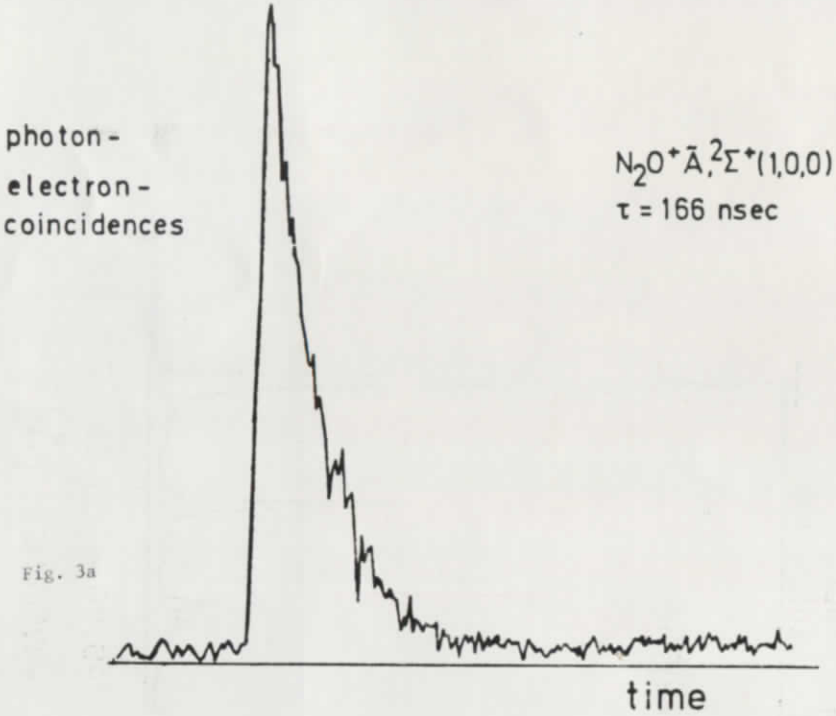
photon-
electron-
coincidences
$N_2O^+ \tilde{A}, {}^2\Sigma^+ (1,0,0)$
$\tau = 166$ nsec
time

Fig. 3a

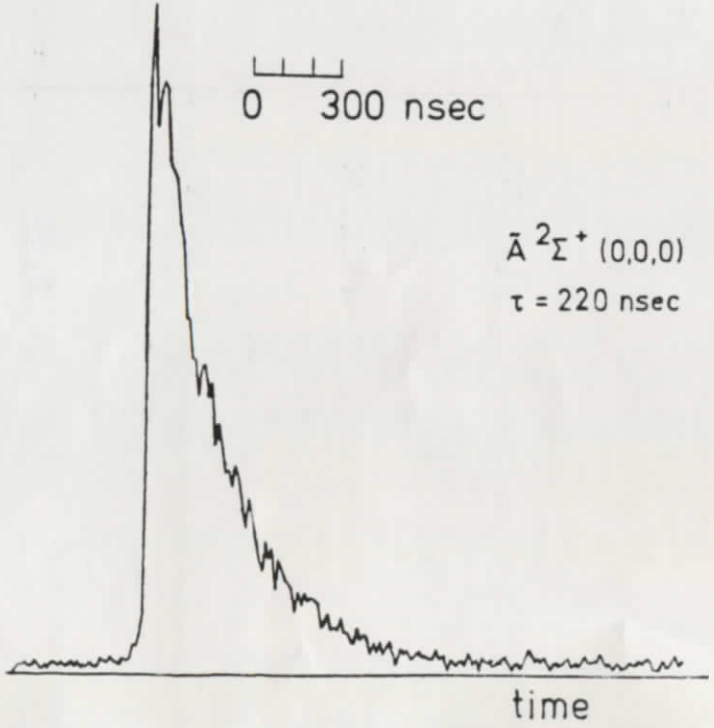
0 300 nsec
$\tilde{A}\ {}^2\Sigma^+ (0,0,0)$
$\tau = 220$ nsec
time

Fig. 3b