

ELECTRON INDUCED EMISSION OF NITROUS OXIDE IN THE UV-VIS SPECTRAL RANGE

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Abstract. The electron impact excitation of N_2O was studied using the crossed electron-molecular beams method. Optical emission spectrum initiated by 50 eV electron impact was recorded within the range 200–700 nm. Main emission bands arise from excited ion state N_2O^+ ($\text{A}^2\Sigma$) and dissociative excitation into N_2^+ ($\text{B}^2\Sigma_u^+$). The rotationally un-resolved excitation-emission cross sections for selected ion transitions were scaled to absolute values and their dependence on electron energy was determined. Several of them were determined for the first time.

Keywords: nitrous oxide, emission, spectrum, electron, excitation, fluorescence.

1. Introduction

Nitrous oxide has been the aim of studies for many years for wide variety of reasons. Its role in the chemistry of the upper atmosphere is considered to be significant due to its contribution to ozone decomposition [1, 2]. The atmospheric chemistry is also a field where spectroscopic data and cross sections are critical. It is important in the field of astrophysics [3] as well as used in many technological applications such as N_2O lasers [4, 5]. Dissociation of nitrous oxide leads to production of various metastable fragments making it interesting for plasma and electrical discharges applications [6, 7].

The excitation of nitrous oxide by electron impact leads to various products. The most prominent one is N_2O^+ ($\text{A}^2\Sigma$). Other excited products created via dissociative excitation are significantly less prominent [8]. In the UV-VIS spectral region it is possible to detect NO ($\text{B}^2\Pi$) but its emission cross section at 100 eV is approximately 20 times smaller than the emission cross section of N_2O^+ bands [8]. The initial excitation of the N_2O molecule is an optically allowed transition leading to repulsive state of N_2O [9]. Van Sprang [9] also reported presence of N_2^+ with its typical 391.4 nm spectral band at 100 eV. Other products of dissociative excitation emit light mostly in the IR region such as OI multiplets at 777.4 nm and 844.7 nm and NI multiplets at 821.1 nm and 869.1 nm or in the VUV region which are outside of the spectral area of this study.

Spectroscopic studies aimed at electron impact in gas phase were done in the past focusing on excitation cross sections [9, 10] and were mostly done in the visible spectral region. The vacuum UV region was studied by Sroka and Zietz [11] and later Malone et al. who evaluated cross sections for the VUV transitions in the absolute scale [12]. Michelin et al. [13] theoretically evaluated the elastic and excitation cross sections for electron impact on nitrous oxide.

Kawahara et al. [14] used an electron energy loss experimental technique to evaluate excitation of the C and D electronic states in nitrous oxide. Even though the emission of nitrous oxide has been studied well, the published absolute values of cross sections are often published only as a scattered values for selected energies. In this work we report whole curves: energy dependent cross sections for the emission cross section of the vibrationally resolved transitions of N_2O^+ ($\text{A}^2\Sigma - \text{X}^2\Pi$).

2. Experiment

The experimental apparatus used for this study was described in detail in [15–17]. A simple scheme of the device is shown in the figure 1. The electron beam was generated by trochoidal electron monochromator with heated tungsten filament used as electron source [18]. The energetic resolution of the electron beam was approximately 300 meV and the electron current measured by the faraday cup was 900 nA and was within 5% of this value in the range from 4 eV up to 100 eV. The electron beam is perpendicular to the molecular beam which is formed by an effusive capillary - the gas entering the capillary has the ambient temperature. The concentration of molecules in the beam was kept low enough to only allow binary electron-molecule collisions. This was tested by measurement of signal intensity dependance on gas pressure in the capillary. The measurements were done at pressures where this dependance is strictly linear. The background pressure measured in the vacuum chamber outside of the molecular beam was 10^{-2} Pa. The optical system of mirrors and lenses guides the photons emitted during deexcitation out of the vacuum chamber and focuses the beam onto the entrance slit of the optical monochromator. A thermoelectrically cooled photomultiplier working in the photon counting regime serves as a detector with noise less than 3 counts per second.

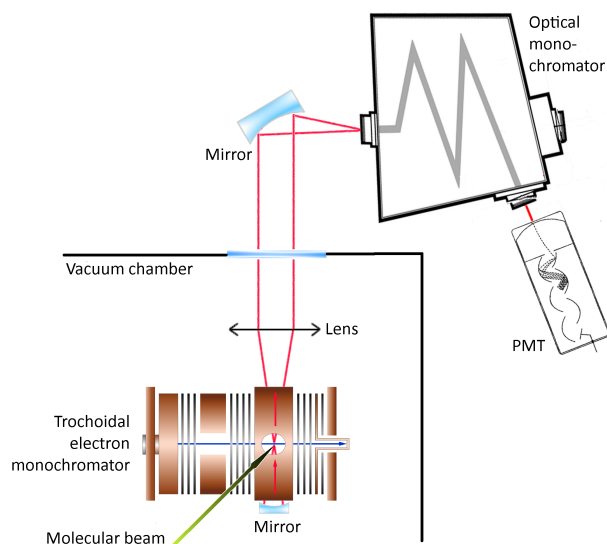


Figure 1. Simple scheme of the crossed beams experimental apparatus. Photon beam is shown in red, electron beam in blue and molecular beam in green. The photomultiplier (PMT) working in the photon counting regime is used as detector. The figure taken from [15] is updated to reflect some technical modifications.

The electron energy was calibrated by measurement of the emission cross section energy dependence of the (0,0) band of N₂ (C³Π_u - B³Π_g) at 337 nm and emission line of He I (1s2p³P_{1,2}⁰ - 1s4d³D_{1,2,3}) 447.14 nm which are created by electron impact. The N₂ (C³Π_u - B³Π_g)(0,0) cross section exhibits a pronounced peak at 14.1 eV. The cross section for the He I (1s2p³P_{1,2}⁰ - 1s4d³D_{1,2,3}) transition exhibits a steep threshold at 23.736 eV. Optical resolution was experimentally determined by measurement of the Ar 294.3 nm line width, which was approximately 0.7 nm at 200 μm width of entrance and output optical monochromator slits. Further increasing the optical resolution did not provide any significant improvement due to reduction of the signal-to-noise ratio.

3. Emission spectrum

The emission spectrum was measured at the incident electron energy of 50 eV in the spectral range from 200 nm to 700 nm. The Figure 2 represents overview spectrum with low resolution and high sensitivity in order to identify the emission bands. In this range most of the bands correspond to deexcitation of excited ion state N₂O⁺ (A²Σ) to the electronic ground ion state (X²Π). The wide bump between 550 nm and 700 nm is an artefact - background radiation of the tungsten filament serving as electron beam source that was able to reach the detector despite the shielding. According to van Sprang [9] there is NO (B²Π - X²Π) system present at the wavelengths below 300 nm. In our spectrum the signal intensity in this region was not high enough to distinguish possible photon signal from the noise. Also, according to [9] the N₂⁺ band at 391.4 nm was present in the spectrum measured at

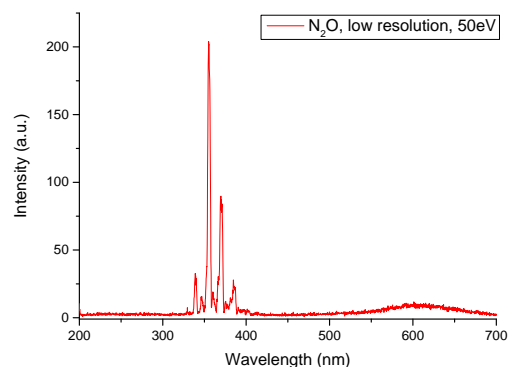


Figure 2. Overview emission spectrum of nitrous oxide induced by 50 eV electrons impact corrected for apparatus spectral sensitivity.

100 eV. In our spectrum measured at 50 eV there is faint signal increase at this wavelength and its vicinity as well. This is in agreement with previous studies reporting the emission of dissociative excitation products of nitrous oxide to be significantly less prominent than N₂O⁺ (A²Σ - X²Π).

We have recorded the spectrum of the nitrous oxide with increased resolution in the range from 330 nm to 410 nm (Figure 3). In the spectrum we were able to recognise individual peaks corresponding to various electron-vibronic transitions. These revealed two distinctive band heads for each transition which were identified according to the [19]. Due to limited resolving power of the spectrometer and low signal strength, we were not able to resolve the rotational transitions within the electron-vibronic bands. The spectrum is corrected for spectral sensitivity of the experimental apparatus. Since the nitrous oxide molecules have ambient temperature, the kinetic energy of the molecule after electron impact ionization and excitation does not change significantly and as the lifetime of the N₂O⁺ (A²Σ) is approximately 230 - 260 ns [9] the produced ions at 300 K will travel approximately 0.1 mm before emission. That is well within the field of view limit of the used experimental device (3 mm) meaning that only negligible portion of the signal might be lost.

4. Emission cross sections

For the six most intensive electron-vibronic transitions of N₂O⁺ (A²Σ - X²Π) the rotationally un-resolved emission cross sections as a function of electron energy were determined with 1 eV electron energy step. The threshold of N₂O⁺ (A²Σ - X²Π) (0,0,0) → (0,0,0) corresponds to the value 16.4 eV published by van Sprang [9]. The cross sections were recorded by measuring the spectral band intensity as a function of incident electron energy. The cross section curves are shown in the figures 4 and 5. The emission cross section curves were calibrated to the absolute scale

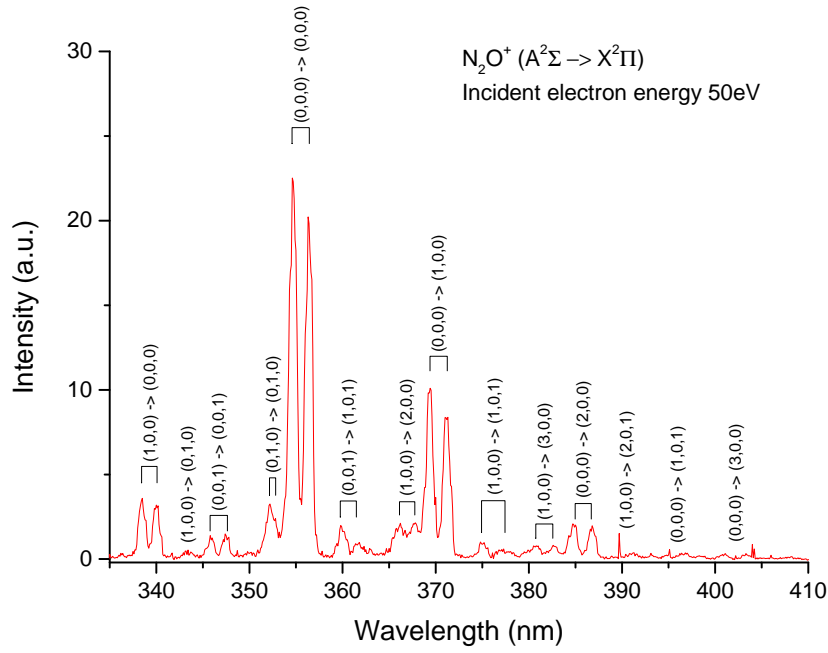


Figure 3. Part of the emission spectrum consisting of various electron-vibronic transitions of nitrous oxide ion.

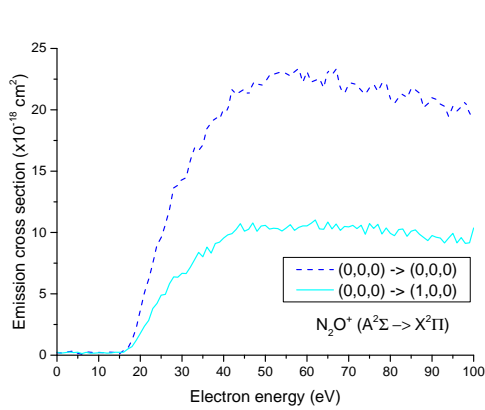


Figure 4. Emission cross sections in the absolute scale for the two most intensive vibronic N_2O^+ transitions.

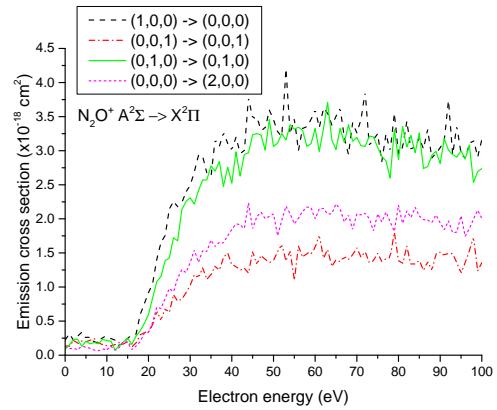


Figure 5. Emission cross sections in the absolute scale for other intensive vibronic N_2O^+ transitions.

by normalizing the measured $(0,0,0) \rightarrow (0,0,0)$ relative curve to the cross section value published by van Sprang [9]. Then the spectrum intensity was adjusted to fit the value of the cross section at 50 eV and all the other cross section curves were normalized according to the values of spectrum intensity at the corresponding wavelengths. The accuracy of such cross section curve determination method assumes that the shape of the molecular spectral band does not change with electron energy significantly. The uncertainty of the measured emission cross sections is influenced by several factors.

The largest effect on the uncertainty in the cross sections is the spectral intensity calibration process. Our data are anchored to the mentioned cross section

value published by van Sprang [9] who claims systematic uncertainty of 15%. This uncertainty leads to a scaling factor affecting all data points. The uncertainty of the spectrometer is based mostly on detector sensitivity and it is between 20% for short wavelengths up to 250 nm and 5% for higher wavelengths. The variations of the electron beam current and molecular beam pressure were less than 5%. Each cross section measurement was repeated several times and the stochastic error in intensity was approximately 5%. Variations of these values affect the final cross section value linearly. From the figures 4 and 5 it can be seen that ratio between the vibronic levels is more or less constant especially within the upper half of the studied energy range. This is in agreement with [20] and [9].

Transition	This work	[10]	[9]
(0,0,0) → (0,0,0)	17.80	15.5	17.8
(0,0,0) → (1,0,0)	7.70	10.2	9.02
(1,0,0) → (0,0,0)	2.80	2.3	2.96
(0,0,1) → (0,0,1)	2.05	-	1.22
(0,1,0) → (0,1,0)	1.65	-	-
(0,0,0) → (2,0,0)	1.50	2.6	2.15

Table 1. Comparison of the cross section values at 100 eV for various vibrational transitions of N₂O⁺ (A²Σ - X²Π). The values are shown in $\times 10^{-18}$ cm².

In the table 1 the cross section values at 100 eV electron energy are compared to previously published ones. The agreement between the determined values at 100 eV is good for the first three transitions and slightly worse for the rest of them. That can be partially explained by lower intensity of these bands and worse signal-to-noise ratio. Generally present values are in good agreement with the earlier observations. The emission cross section for the transition N₂O⁺ (A²Σ - X²Π) (0,1,0) → (0,1,0) was determined for the first time and most of the other cross sections were known only for several discreet energy values. In this work we managed to determine them in the energy range from threshold to 100 eV.

The data from the figures 4 and 5 are tabulated as supplement tables 2 and 3 at the end of the paper for easier further processing.

5. Conclusions

The emission spectrum of nitrous oxide induced by electron impact was studied by crossed beams method. The spectrum induced at 50 eV consists of very intensive electron-vibronic transitions of N₂O⁺ (A²Σ - X²Π) and weak N₂⁺ (B²Σ_u⁺) band. Emission cross sections were determined as a function of electron impact energy in the range from threshold to 100 eV for the six most intensive bands. The values at 100 eV were compared to previously published values.

Acknowledgements

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Electron energy (eV)	(0,0,0) - - (0,0,0)	(0,0,0) - - (1,0,0)	(1,0,0) - - (0,0,0)	(0,0,1) - - (0,0,1)	(0,1,0) - - (0,1,0)	(0,0,0) - - (2,0,0)
1	0.175	0.171	0.314	0.149	0.096	0.121
2	0.305	0.211	0.221	0.233	0.102	0.218
3	0.251	0.261	0.279	0.233	0.080	0.162
4	0.371	0.211	0.337	0.130	0.134	0.210
5	0.142	0.241	0.244	0.205	0.118	0.194
6	0.076	0.130	0.268	0.168	0.102	0.218
7	0.305	0.231	0.186	0.186	0.075	0.242
8	0.175	0.161	0.175	0.168	0.064	0.170
9	0.284	0.171	0.279	0.233	0.091	0.154
10	0.229	0.201	0.256	0.214	0.080	0.137
11	0.207	0.211	0.244	0.205	0.134	0.137
12	0.218	0.171	0.221	0.075	0.069	0.154
13	0.273	0.181	0.128	0.140	0.112	0.186
14	0.207	0.241	0.186	0.196	0.203	0.154
15	0.120	0.231	0.244	0.251	0.187	0.202
16	0.382	0.241	0.303	0.158	0.080	0.121
17	0.567	0.502	0.303	0.279	0.134	0.170
18	1.211	0.693	0.594	0.354	0.198	0.299
19	2.203	1.205	0.756	0.466	0.326	0.339
20	3.665	1.777	0.919	0.596	0.331	0.339
21	5.115	2.359	1.047	0.838	0.481	0.436
22	6.184	2.831	1.408	1.080	0.705	0.655
23	7.482	3.804	1.652	1.155	0.684	0.501
24	8.998	4.216	1.757	1.388	0.833	0.695
25	9.533	4.888	2.141	1.425	0.978	0.622
26	10.656	4.959	2.258	1.723	0.930	0.889
27	11.867	5.822	2.176	1.677	1.127	0.792
28	13.667	6.384	2.234	2.133	1.256	0.824
29	13.852	6.354	2.397	2.254	1.213	0.913
30	14.375	6.675	2.490	2.310	1.357	1.026
31	14.441	6.655	2.688	2.217	1.544	1.180
32	15.870	7.167	2.933	2.412	1.362	1.123
33	16.895	7.769	2.921	2.571	1.533	1.285
34	16.677	8.382	2.677	2.571	1.517	1.115
35	17.135	8.020	2.618	2.776	1.688	1.172
36	18.520	8.813	3.165	2.701	1.592	1.317
37	18.902	8.321	3.061	2.841	1.656	1.245
38	19.393	9.104	3.270	2.478	1.646	1.430
39	19.229	9.215	3.107	2.757	1.752	1.503
40	20.058	9.546	3.002	2.524	1.843	1.325
41	19.949	9.807	3.200	2.981	1.929	1.309
42	21.694	9.907	2.967	2.627	1.913	1.245
43	21.247	10.249	2.979	2.943	1.854	1.277
44	21.487	10.720	3.782	2.971	2.233	1.204
45	21.683	10.108	3.468	3.232	1.854	1.527
46	21.192	10.269	3.491	3.251	2.030	1.325
47	22.185	10.781	3.305	3.232	2.100	1.463
48	22.174	10.098	3.317	3.009	2.004	1.406
49	21.934	10.530	3.596	3.456	2.036	1.358
50	22.294	10.580	3.456	3.064	2.073	1.390

Table 2. Emission cross section values as a function of energy for the measured electron-vibronic transitions of N₂O⁺ (A²Σ - X²Π) in the range 1 - 50 eV. The values are shown in $\times 10^{-18}$ cm².

Electron energy (eV)	(0,0,0) - - (0,0,0)	(0,0,0) - - (1,0,0)	(1,0,0) - - (0,0,0)	(0,0,1) - - (0,0,1)	(0,1,0) - - (0,1,0)	(0,0,0) - - (2,0,0)
51	22.796	10.279	3.270	3.111	1.752	1.519
52	22.883	10.349	3.212	3.251	1.977	1.632
53	23.079	10.319	4.201	3.158	2.185	1.382
54	22.970	10.118	3.247	3.381	2.078	1.535
55	22.992	10.369	3.468	3.316	1.929	1.099
56	22.752	10.640	3.002	3.344	2.009	1.600
57	23.123	10.168	3.340	3.297	2.110	1.438
58	23.363	10.409	3.352	3.064	2.175	1.511
59	22.250	10.540	3.456	3.102	2.164	1.487
60	23.112	10.540	3.608	3.325	1.998	1.576
61	22.261	10.750	3.340	2.990	2.148	1.770
62	22.403	11.021	3.619	3.325	2.153	1.422
63	22.545	10.299	3.561	3.707	2.068	1.552
64	21.792	10.259	3.375	3.158	2.078	1.301
65	23.199	10.851	3.503	3.018	2.217	1.398
66	22.861	10.299	3.631	3.325	2.142	1.374
67	23.319	10.690	3.189	3.120	1.955	1.455
68	21.738	10.168	2.944	3.381	2.057	1.406
69	21.323	10.489	3.410	3.139	1.843	1.471
70	22.087	10.459	3.258	3.195	2.073	1.576
71	22.229	10.580	3.456	3.074	2.057	1.438
72	21.978	10.319	3.864	3.064	2.084	1.519
73	21.585	10.590	3.072	3.213	2.004	1.358
74	21.247	9.857	3.165	3.204	1.822	1.382
75	21.792	10.730	3.247	3.046	2.073	1.495
76	22.098	10.329	2.839	2.915	1.955	1.374
77	21.498	10.670	3.247	2.850	2.100	1.414
78	22.163	9.877	2.991	2.599	1.955	1.430
79	22.163	10.369	3.549	3.307	1.817	1.802
80	20.898	9.927	2.956	2.869	2.201	1.382
81	20.516	9.737	3.049	3.353	1.934	1.333
82	21.018	10.239	3.433	3.055	2.116	1.600
83	21.312	10.289	3.014	3.223	2.020	1.317
84	20.963	9.686	3.061	2.971	2.169	1.342
85	21.705	10.108	3.189	3.260	2.041	1.390
86	21.629	10.218	3.026	2.738	1.988	1.245
87	21.356	9.857	3.317	2.766	1.982	1.382
88	20.211	9.596	2.886	2.934	1.945	1.236
89	20.451	9.335	2.967	2.990	2.057	1.487
90	21.018	9.757	3.037	2.813	1.939	1.511
91	20.843	9.616	3.154	3.176	1.838	1.455
92	20.462	9.546	3.736	3.009	1.971	1.495
93	20.287	9.144	2.944	2.943	1.795	1.487
94	19.458	9.546	3.363	2.906	1.806	1.358
95	20.287	9.927	2.967	2.999	2.046	1.196
96	19.905	9.154	2.874	2.878	1.747	1.358
97	20.243	9.586	3.096	3.083	1.854	1.527
98	20.691	9.114	3.165	2.533	1.998	1.738
99	19.676	9.164	2.909	2.692	2.126	1.236
100	19.480	10.369	3.165	2.738	2.009	1.358

Table 3. Emission cross section values as a function of energy for the measured electron-vibronic transitions of N_2O^+ ($A^2\Sigma - X^2\Pi$) in the range 51 - 100 eV. The values are shown in $\times 10^{-18} \text{ cm}^2$.