



## Vibrationally excited state spectroscopy of radicals in a supersonic plasma

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### Abstract

A plasma source based on a multilayer discharge geometry in combination with a time-of-flight REMPI experiment is used to study rotationally cold spectra of highly excited vibrational states of mass selected radicals. The rovibrational state distributions upon discharge excitation are characterised for the example of NO for ground state vibrational levels up to  $v'' = 18$ . Whereas rotational temperatures are lower than 50 K, a vibrational temperature of  $T_{\text{vib}} = 6700 \pm 700$  K is found. © 2001 Elsevier Science B.V. All rights reserved.

### 1. Introduction

Adiabatically cooled plasmas are routinely used to simplify the spectroscopy of highly reactive species. Several techniques have been proposed in the past to achieve stable supersonic plasmas, generally by combining ablation, photolysis, pyrolysis, discharge or electron impact techniques and molecular beam or jet expansions [1–11]. Recently, it was shown that a supersonic plasma also can be used to obtain *rotationally cold* spectra of *vibrationally excited* molecules [12,13]. This might be important to study vibrational anharmonicity and intramolecular vibrational energy redistribution or as a starting point in scattering experiments or isotope separation. If there is no need for preparing a vibrational distribution state selectively, a

supersonic plasma may conveniently replace an additional laser system, which is normally required for experiments starting from vibrationally excited systems [14–16].

The current work presents a quantitative extension of the results discussed in [12] for the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic system of NO, using a different source that is essentially a pinhole variant of a planar geometry in which the plasma is generated in the throat of a slit nozzle [10]. Upon discharge excitation a clear decrease of the initial  $v'' = 0$  population is observed. The resulting energy redistribution is studied for vibrational levels up to  $v'' = 18$ , i.e., as much as 3.8 eV above the vibrational ground state.

### 2. Experiment

A cross-section of the source that is used to achieve rotationally cold spectra of vibrationally

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excited species is shown to scale in Fig. 1. A pulsed discharge is confined to a small region upstream of the actual expansion by striking a negative HV pulse from the outer plate via a ceramic insulator to a grounded plate that is mounted on a ceramic body shielding a pulsed valve (general valve). Special attention has been paid to maintain a flat voltage/current profile during the discharge pulse. For this a fast HV switch (Behlke) is used to generate an intense ( $-1150$  V) and stable  $100 \mu\text{s}$  long HV pulse within a  $160 \mu\text{s}$  long gas pulse. In this configuration the actual expansion is not influenced by the discharge, which makes low final temperatures possible; in a previously reported study on vibrationally excited CF (0.2% in He [13]) values of  $T_{\text{rot}} \approx 10$  K were achieved for levels up to

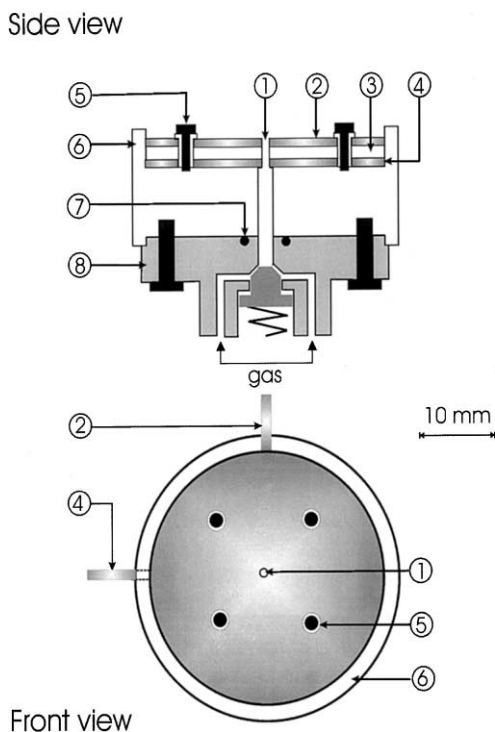


Fig. 1. Cross-section of the pinhole discharge nozzle. The gas is expanded through a circular orifice ( $400 \mu\text{m}$ ) [1] consisting of a stainless steel cathode [2] that is put on negative voltage, a ceramic insulator [3] and an anode [4] that is grounded. The electrodes and insulator are mounted by electrically isolated screws [5] to the body of the nozzle [6]. The latter is connected via an O-ring [7] to an electromagnetically driven valve [8]. Apart from the expansion channel, the figure is drawn to scale.

$v'' = 12$ . In the present experiment a less diluted mixture of 5% NO in He is expanded with a backing pressure of 3 bar.

The discharge nozzle is used in a new molecular beam apparatus (Fig. 2) incorporating a time-of-flight mass spectrometer (TOF-MS) in a McLaren configuration [17]. The source chamber is kept at a pressure better than  $10^{-4}$  mbar during beam operation by a  $1000 \text{ ls}^{-1}$  diffusion pump. A 1 mm skimmer is used as inlet into the detection chamber where the molecular beam expansion is intersected by a laser beam approximately 25 cm downstream in the acceleration region of the TOF-MS. A turbo molecular pump (Alcatel ATP400) is used to maintain a pressure of  $2 \times 10^{-5}$  mbar at this point. The skimmer is surrounded by two electrodes that are put on a positive and negative potential to prohibit ions produced in the plasma from entering the detection chamber. A slotted liquid nitrogen cooled shield around the TOF-MS unit is used to suppress possible background signal due to pump oil. The vibrationally excited NO radicals are detected by recording the  $\text{NO}^+$  mass signal in the TOF-MS after resonant ionisation, using a one-colour (1 + 1) REMPI scheme. The resulting signal on the MSP detector is amplified and recorded in a boxcar integration scheme. The whole experiment runs at 10 Hz. A delay genera-

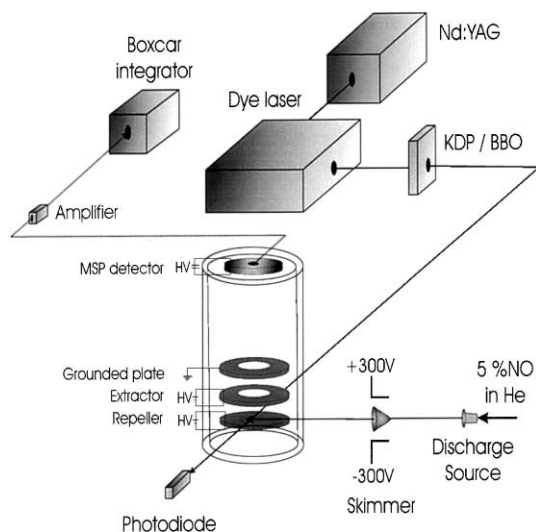


Fig. 2. Schematic of the experimental set-up.

tor is used to synchronise gas, discharge and laser pulse.

For the excitation the frequency doubled output of a Nd:YAG pumped dye laser is used. After passing a KDP or BBO crystal typical linewidths amount to  $0.10 \text{ cm}^{-1}$ . The pulse energy of the laser is measured with a photodiode, yielding values between 200 and  $900 \mu\text{J}/\text{pulse}$ , depending on spectral region. For the present study measurements have been performed in three wavelength regions; around 226, 280 and 320 nm.

### 3. Results and discussion

Upon discharge excitation a clear decrease in the  $v'' = 0$  ( $X^2\Pi$ ) population is observed. Using a one-colour (1 + 1) REMPI scheme around 226 nm a depopulation of  $\sim 75\%$  is found for the experimental conditions given before. The subsequent population redistribution allows the observation of a series of vibrationally excited bands in the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic system. In Fig. 3 an overview is given for the 320 nm region, showing transitions starting from vibrationally excited electronic ground state levels as high as  $v'' = 18$ . The experimental spectra are well reproduced using the spectroscopic constants given in [18]. This is shown in Fig. 3 as well. Whereas the vibrational distribution clearly differs from the situation without discharge, rotational temperatures are found as low as about 10 K at  $v'' = 0$  and as high as 45 K at  $v'' > 4$ . This can be understood when ground state vibrational levels are populated from higher electronic states that are excited during the discharge pulse. The subsequent relaxation of rotational energy is expected to be dominated by NO–He collisions, whereas the relaxation of the NO vibration is governed by NO–NO collisions and is consequently much slower.

More quantitative information on these relaxation processes is available from several other studies. A crossed molecular beam experiment studying state-to-state energy transfer for inelastic collisions of NO  $X^2\Pi_{1/2}$  ( $v = 20$ ,  $J = 1/2$ ) and He [19] concludes in agreement with ab initio calculations that  $v''$  is conserved and that the rotational energy transfer occurs with a rate corresponding to

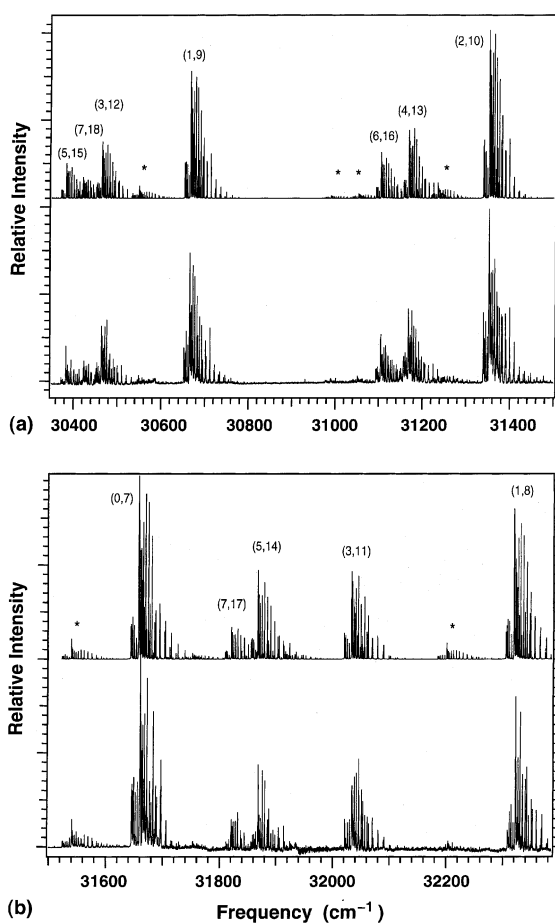


Fig. 3. One colour (1 + 1) REMPI spectrum around 320 nm of vibrationally excited bands of the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic system of NO expanded through a multilayer discharge source. The lower part shows the measured spectrum, the upper part the simulated spectrum taking  $T_{\text{rot}} = 45 \text{ K}$ . In some cases the second spin-orbit component is visible, which is indicated by a \* in the simulated spectrum.

a collision cross-section of about  $20 \text{ \AA}^2$  [19]. Experiments extending these measurements to temperatures between 15 and 300 K report a similar value [20]. A study of the state-to-state collisional energy transfer between NO ( $v'' = 8-25$ ,  $J''$ ) and NO (300 K) in bulk shows that the rotational (and spin-orbit) energy transfer occurs essentially independent of  $v''$  with an overall rate that corresponds to a collision cross section of about  $60 \text{ \AA}^2$  [21]. For vibrational levels up to  $v'' = 14$  the rate of vibrational energy transfer was found to be

$0.011 v'' \text{Å}^2$  [22]. This linear dependence suggests that collisional relaxation occurs through one-quantum energy transfer. For higher  $v''$  levels multiquantum relaxation becomes relevant, raising the cross section more rapidly to  $2.2 \text{Å}^2$  for  $v'' = 25$ . These numbers indicate that for the levels studied here vibrational relaxation is several orders of magnitudes slower than rotational relaxation. This is demonstrated in Fig. 4 for the  $(v', v'') = (0, 7)$  band that is visible only after discharge excitation. A Boltzmann plot yields an average rotational temperature of  $T_{\text{rot}} = 45(10) \text{ K}$  for the lower ( $\Omega = 1/2$ ) component. The other component ( $\Omega = 3/2$ ) is much weaker as spin-orbit cooling is expected to be effective [23], i.e., with  $A_v'' \approx 125 \text{ cm}^{-1}$  [24] only a minor part of the population will be left in the higher level. The global rotational temperature of the upper component amounts to  $T_{\text{rot}, \Omega=3/2} = 68(10) \text{ K}$ , only slightly above the value found for the lower component. This extracted value for the fine structure temperature ( $T_f = 40 \text{ K}$ ) turns out to be essentially the same as  $T_{\text{rot}, \Omega=1/2}$  and supports the experimental suggestion in [19] of a more facile transfer between the two spin-orbit manifolds upon vibrational excitation. This difference is much larger in the case of the origin band transition  $(v', v'') = (0, 0)$  where the

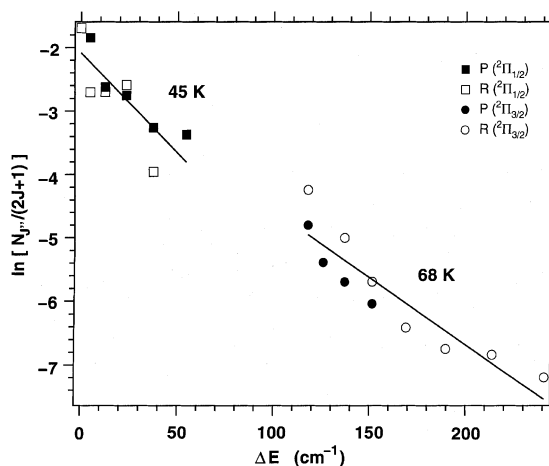


Fig. 4. The Boltzmann plots for the  $\Omega = 1/2$  and  $3/2$  spin-orbit components of the  $(v', v'') = (0, 7)$  band of the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic transition of NO, yielding rotational temperatures of 45(10) and 68(10) K, respectively.

spin-orbit components are far from local equilibrium ( $T_{\text{rot}, \Omega=1/2} = 20(4) \text{ K}$  and  $T_{\text{rot}, \Omega=3/2} = 235(35) \text{ K}$  – also without plasma), an effect that has been described in detail before in [25,26]. There it was concluded that in a He expansion a bottleneck appears at low  $J$  values in the upper spin-orbit component as a consequence of the different energy transfer rates within and in between the spin-orbit manifolds  $T_f$  is found to be 72(5) K, causing  $T_{\text{rot}, \Omega=3/2}$  to be of the order of 240 K. In the case of the (0,7) levels the populations will be much less and the minor difference in rotational temperature may be simply the effect of the higher internal energy in the upper state.

In order to study the relative vibrational population distribution in a more quantitative way, the power dependence ( $P^n$ ) of the ion current of the observed (1+1) REMPI signal has been measured. Without a lens it is found that  $n \approx 2$  for all bands, indicating that saturation does not take place<sup>1</sup>. Consequently, the relative population in a rovibronic band  $N(v'', J'')$  is determined from the simulation of the intensity profile of the power normalised spectra for  $\Omega = 1/2$ , explicitly taking into account Franck–Condon ( $q_{v', v''}$  [27]) and Hönl–London ( $S_{J', J''}$  [28]) factors for the  $A-X$  system<sup>2</sup>. Subsequent normalisation with respect to the origin band yields the population density plot as shown in Fig. 5 on a logarithmic scale. At this point it is assumed – as in previous work – that the ionisation cross-section is not [29,30] or only slightly [31]  $v''$ -dependent. The latter study estimates that by ignoring complications due to possible predissociation in the A-state or dissociative resonances in the ionisation continuum an error – if any – of maximum a factor 2 might arise. Systematic measurements will be necessary to get more detailed information, but it is unlikely that such effects could change the present conclusions.

Relative population densities have been determined for all vibrational ground state levels up to  $v'' = 18$ , apart from  $v'' = 1, 2$  and 5 that were not directly or poorly accessible in a one colour (1+1)

<sup>1</sup> With a focusing lens ( $f = 250 \text{ mm}$ ) it is found that  $n = 1$ .

<sup>2</sup> The Franck–Condon and Hönl–London factors in the ionisation step are not related with  $N(v'', J'')$ .

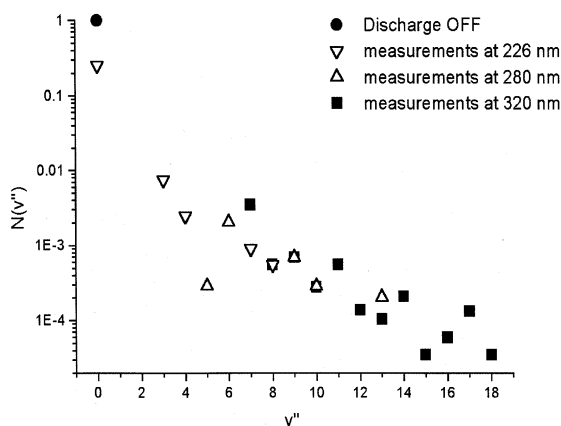


Fig. 5. The relative population density of subsequent vibrational levels upon discharge excitation in three frequency ranges ( $\nabla = 226$  nm,  $\triangle = 280$  nm,  $\blacksquare = 320$  nm) normalized on the  $v'' = 0$  population without discharge ( $\bullet$ ). For  $6 \leq v'' \leq 18$  a fit for the vibrational temperature yields  $T_{\text{vib}} = 6700 \pm 700$  K.

REMPI scheme within the available frequency range. However,  $v'' = 1$  and  $2$  have been determined in [12] employing  $(2 + 1)$  REMPI. A direct comparison between the two experiments is not possible as too many expansion parameters differ; in [12] Ar or Ne expansions are used and the discharge strikes directly to a piezo driven valve. However, it is expected that the  $v'' = 1$  and  $2$  levels profit most from the depopulation of the vibrational ground state, even though the absolute NO concentration might decrease as a consequence of direct ionisation or fragmentation upon discharge excitation. Future work to determine  $\frac{N(v''=0)}{N(v''=1)}$  and  $\frac{N(v''=1)}{N(v''=2)}$  will give more insight into the actual depletion factor.

As far as there exists an overlap in the density calculations because of bands starting from the same initial state, the overlap is good and within the estimated uncertainty of 10%. The discrepancy between 226 and 320 nm measurements existing for  $v'' = 7$  is most likely due to the different (diagonal and non-diagonal) character of the ionisation schemes. The figure shows that up to  $v'' = 7$  population densities of the order of 0.1–1% are achieved, decreasing to 0.01% of the initial  $v'' = 0$  population without plasma for levels up to  $v'' = 15$ . An interpretation of these numbers for  $6 \leq v'' \leq 18$  (see Fig. 5) yields a vibrational temperature of  $6700 \pm 700$  K.

It is worth noting that this method might be limited to molecules with strongly fluorescing excited states when ground state vibrational levels are populated from electronically excited states by emission only. To check this the sum of the Frank–Condon factors of vibrational levels  $v'$  in fluorescing electronic states to a single  $v''$  ground state level has to be compared with the observed density distribution  $N(v'', J'')$ . As highly vibrationally excited electronic states may predissociate or transfer into an ionic state and as it is unclear how much NO is lost upon plasma excitation, such an analysis will be hard to perform. However, it was found [12] that the relative population densities are pressure dependent, which makes it likely that non-radiative processes are involved as well.

In summary, it is concluded that plasma excitation in combination with a subsequent supersonic expansion is an efficient technique to obtain high resolution spectra of vibrationally excited levels without a severe loss of rotational cooling. The current work presents new insights into the resulting rovibronic state distributions and it is expected that even higher vibrational levels should be accessible in this way.

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