



Measurement of the V–T energy transfer rates of highly excited 2 A 1 NO2

Troy L. Mazely, Randall R. Friedl, and Stanley P. Sander

Citation: The Journal of Chemical Physics **100**, 8040 (1994); doi: 10.1063/1.466797 View online: http://dx.doi.org/10.1063/1.466797 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/100/11?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Measurement of rotational energy transfer rates for HD (v=1) in collisions with thermal HD J. Chem. Phys. **85**, 810 (1986); 10.1063/1.451842

V–V energy transfer from highly vibrationally excited azulene to CO2 J. Chem. Phys. **83**, 6049 (1985); 10.1063/1.449590

Enhancement of chargetransfer reaction rate constants by vibrational excitation at kinetic energies below 1 eV

J. Chem. Phys. 79, 265 (1983); 10.1063/1.445566

Laser double resonance measurements of vibrational energy transfer rates and mechanisms in HF(v = 2) J. Chem. Phys. **77**, 3974 (1982); 10.1063/1.444360

Measurement of the VV energy transfer rate from CO(v = 2) using tunable parametric oscillator excitation Appl. Phys. Lett. **22**, 367 (1973); 10.1063/1.1654676



Measurement of the V-T energy transfer rates of highly excited ${}^{2}A_{1}$ NO₂

Troy L. Mazely,^{a)} Randall R. Friedl, and Stanley P. Sander Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109

(Received 24 June 1993; accepted 18 February 1994)

Production of electronic ground state NO₂ (²A₁) from 248 nm photolysis of HNO₃ was detected by laser induced fluorescence (LIF). A growth in the LIF signal was observed following the photolysis and has been interpreted as the relaxation of NO₂ through the higher vibrational levels of the $X(^2A_1)$ state; an energy region where the probe laser photodissociates the NO₂ instead of inducing fluorescence. The rate coefficients for NO₂ relaxation through these high vibrational levels were determined by fits of time resolved LIF signal to a stepladder kinetic model. The results of the kinetic analysis suggest that the observed relaxation begins at the ²B₂ threshold near 9500 cm⁻¹ and extends downward through approximately 5 vibrational levels of the ground electronic surface. The derived quenching rate coefficients (in units of 10^{-12} cm³ molecule⁻¹ s⁻¹) are 0.51±0.05, 1.0±0.1, 1.4 ± 0.2 , 2.6 ± 0.6 , and 8.7 ± 1.1 for Ar, He, N₂, O₂, and CO₂ collision partners, respectively. The discrepancies between these coefficients and previous literature values are rationalized in terms of a dependence of the vibrational relaxation rate on total internal energy.

INTRODUCTION

The visible absorption and fluorescence spectra of NO₂, extending from 400 nm to beyond 700 nm, are quite complicated due to the mixing between the high vibrational levels of the $X(^{2}A_{1})$ electronic state with the $A(^{2}B_{2})$ and, to a lesser degree, the $B(^{2}B_{1})$ electronic states.¹ The extensive mixing between these electronic levels has made vibrational state specification of NO₂ difficult near, and beyond, the $^{2}B_{2}$ threshold which occurs approximately 9500 cm⁻¹ above the ground state.²

Attempts to simulate the relaxation kinetics of electronically excited $NO_2(NO_2^*)$ have often employed a simplified population distribution that involves a discrete set of equally spaced levels.^{3,4} In these models, the NO_2^* is allowed to relax collisionally to adjacent excited states or decay radiatively directly to vibrational levels in the ${}^{2}A_{1}$ state. Above the ${}^{2}B_{2}$ threshold collisional quenching predominates over radiative decay provided the total pressure is above 50 mTorr.⁵ Near the ${}^{2}B_{2}$ threshold, electronic energy is transferred to the vibrational modes of the ${}^{2}A_{1}$ state; the resulting electronic ground state NO₂ is highly vibrationally excited (NO^{\dagger}₂). A change in the relaxation mechanism occurs as the excited NO_2 acquires more 2A_1 character because the deactivation is through well defined vibrational states of the ground electronic manifold instead of through a dense manifold of mixed electronic and vibronic states.

Experimental attempts to investigate the kinetics of NO₂ relaxation have relied mainly on observations of excited NO₂ emission. Measurements of visible emission lifetimes following optical excitation of NO₂, for instance, have led to a greater understanding of the electronic relaxation of NO₂^{*}.^{3,6-13} Rate coefficients for electronic quenching of NO₂^{*} have been measured to be roughly gas kinetic, i.e., 10^{-10} cm³ molecule⁻¹ s⁻¹, with only a slight dependence on the collision partner.

Vibrational deactivation of electronic ground state NO₂ has been investigated by a number of techniques. The earliest attempts involved monitoring the time resolved infrared chemiluminescence of NO₂⁺ arising from the reaction of NO with both O and O₃. By measuring the emission in the 3.7 μ m band of NO₂, Golde and Kaufman¹⁴ estimated a rate coefficient for the vibrational relaxation of NO₂ in an Ar carrier gas of approximately 6×10^{-14} cm³ molecule⁻¹ s⁻¹. Although their technique could not yield a precise absolute rate coefficient, it provided meaningful relative rates as a function of buffer gas. Reported values were 55±35, 40±25, 5±2, 2.0±0.5, and 1 for NO₂, NO, O₂, N₂, and Ar, respectively. Unlike the electronic relaxation of NO₂, the Golde and Kaufman results demonstrate that vibrational relaxation is strongly dependent on the collision partner.

Vibrational relaxation has also been studied by observing infrared emission from optically excited NO2. McAndrew et al.¹⁵ inferred vibrational relaxation rate coefficients by measuring the time dependence of various infrared emission bands of NO₂. Based on a multiparameter kinetic fit of the emission in the 6.1–6.8 μ m region ($\Delta v_3 = 1$ transitions), a vibrational quenching rate coefficient of $(1.8\pm0.6)\times10^{-13}$ cm^3 molecule⁻¹ s⁻¹ was reported for He. Relative to the rate coefficient in He, the rates in NO2, CO2, and Xe were determined to be 18 ± 9 , 15 ± 8 , and 1.8 ± 0.8 , respectively. The internal energy distribution of the NO₂ emitting in this band was not derived; presumably the emission contained contributions from a range of excited vibrational levels in the ν_{2} manifold. Larger quenching rate coefficients were derived from emission in the 3–4 μ m region, however, most of the signal in this region was attributed to electronic rather than vibrational components of the relaxation.

A method to probe relaxation of low-lying vibrational levels has been developed by Toselli *et al.*¹⁶ They applied thermal lensing to study NO₂ vibrational relaxation following optical excitation. A rate coefficient of $(5.1\pm1.0)\times10^{-14}$ cm³ molecule⁻¹ s⁻¹ was derived for the relaxation of NO₂(010) in Ar.

8040 J. Chem. Phys. 100 (11), 1 June 1994 0021-9606/94

^{a)}NASA/NRC Resident Research Associate.

of Air content is subject to the terms at. http

Theoretical models of V-T relaxation generally predict that the relaxation rate coefficient scales with total internal energy.^{4,17,18} The model of Schwartz, Slawsky, and Herzfeld (SSH theory)¹⁸ predicts that the relaxation rate should be directly proportional to the vibrational quantum number of the initial level. Recently, Adler-Golden⁴ has presented a treatment specifically for NO₂ in which a density of states argument was employed to obtain a numeric expression for the relaxation rate coefficient as a function of the excess energy of the NO₂. Parameterization of the derived expressions was made by combining existing data on the relaxation of NO₂. The results of this model predict a stronger dependence of the NO₂ relaxation rate on internal energy than SSH theory.

In this study we have obtained information on the vibrational relaxation of NO₂ at energies near the ${}^{2}B_{2}$ threshold by using HNO₃ photolysis as a convenient source of excited NO₂. The photolysis of HNO₃ has been extensively studied at a variety of wavelengths.^{19–31} Although many mechanistic details remain uncertain regarding the photolysis products of HNO₃, especially as a function of wavelength, Reaction (1)

$$HNO_3 + h\nu \rightarrow OH + NO_2 \tag{1}$$

is believed to be the only channel accessed at 248 nm. The deposition of the available excess energy after photolysis, \approx 24 000 cm⁻¹, into the OH and NO₂ photofragments has been studied by a number of investigators. Jacobs et al.,²⁶ Schutter and Kleinermanns,²⁷ Likar et al.,²⁸ and August et al.²⁹ utilized uv laser induced fluorescence to probe the nascent OH rotational and vibrational population distributions. These studies set 5% as an upper limit of the amount of excess energy deposited into OH vibration and rotation. Oh et al.³⁰ observed visible emission from nascent NO₂ and suggested that a significant fraction of the NO₂ photoproduct is electronically excited. The internal energy of the nascent NO₂^{*} photoproduct has been characterized by Miller.³¹ The distribution is broad and ranges from 12 000 to 23 000 cm^{-1} of internal energy with a maximum at approximately 16 000 cm^{-1} for photolysis at 248 nm. These energies, which are well above the threshold of the ${}^{2}B_{2}$ state, indicate that the nascent NO₂ is completely electronically excited.

We have utilized the technique of LIF as a diagnostic for NO₂. Since the threshold for photodissociation of NO₂ is at 25 100 cm⁻¹, the photon energy of the probe laser employed in this study (19 600 cm⁻¹) is sufficient to induce photodissociation of all NO₂ molecules containing more than approximately 5500 cm⁻¹ of internal energy.⁵ Since the nascent NO₂ population is at energies above this value no initial LIF signal is expected and detection of NO₂ by LIF occurs only *after* the nascent population relaxes below 5500 cm⁻¹. We have analyzed the time delay in LIF detection of NO₂ following HNO₃ photolysis in order to quantify the kinetics of the NO₂ relaxation process between 9500 and 5500 cm⁻¹.

EXPERIMENT

A schematic of the experimental apparatus is shown in Fig. 1. HNO_3 vapor was introduced into the flowing system by passing a carrier gas (He, Ar, N₂, O₂, or CO₂) through a bubbler containing pure liquid HNO_3 . The HNO_3 was syn-

thesized by collecting the vacuum distillate of a 50:50 by volume mixture of 95% H_2SO_4 with NaNO₃. The HNO₃ was maintained at 0° C by placing the bubbler in an ice bath. The HNO₃ vapor concentration was determined by optical absorption at 254 nm in a 50 cm long absorption cell upstream of a teflon needle valve (Gilmont). The HNO₃ concentrations derived from the optical measurements agreed well with estimates based on the known vapor pressure of HNO₃. The pressures in the bubbler and absorption cell were controlled by the needle valve and monitored with an MKS Baratron capacitance manometer. All flows rates were determined using calibrated flow meters (Hastings).

The HNO₃ concentration in the quartz photolysis cell was reduced relative to the bubbler by injection of additional buffer gas in an upstream mixing region. The concentration of HNO₃ in the photolysis cell ranged between $(0.08-50)\times10^{14}$ molecule cm⁻³ at total pressures between 0.5 to 10.0 Torr. The flow rate into the cell was varied between 250 to 4000 sccm to insure complete flushing of the photolytic products between photolysis laser shots.

An excimer laser (Questek Model 2240) operating at 248 nm and at a pulse repetition rate of 20–30 Hz was used to photolyze HNO₃. The output of the excimer was weakly focused with a 2000 cm focal length lens. The pump laser optical path through the photolysis cell was defined by 0.86 cm diameter entrance and exit irises. The energy density of the excimer laser ranged from 25 to 150 mJ/cm² per pulse and was monitored with a Joule meter (Scientech P50). Under these conditions the photolytic signal was observed to be linear with laser pulse energy. The fractional dissociation of HNO₃ by each excimer laser pulse was estimated to be $\approx 0.1\%$ based on the HNO₃ absorption cross section at 248 nm and a typical excimer laser fluence of 50 mJ/cm².

A 15 W, pulsed copper vapor laser (CVL: Oxford model CU15A) with a tunable repetition frequency between 6 to 20 kHz was utilized to probe for generated NO₂ by LIF. The 578 nm output from the CVL was eliminated by passage of the beam through two short wave pass filters. The transmitted 511 nm line was directed through a telescope to reduce the diameter of the beam. The weakly convergent beam was then passed through two irises and sent to the photolysis cell. The fraction of NO₂ excited by each probe pulse was estimated to be 0.05%. For some experiments the CVL was replaced by a 10 Hz, 150 mW Nd:YAG laser (Quanta-Ray DCR-1). The optical path of the 532 nm output of the Nd:YAG was similar to that of the CVL.

The LIF signal was detected by a cooled photomultiplier tube (PMT: Burle C31034-02) that was oriented orthogonal to the laser beam axes. The LIF signal was amplified, discriminated, and counted on a multichannel scaler card (MCS: Canberra Accuspec) with a bin width of 5 μ s. A 550 nm long pass filter was placed in front of the PMT to block excimer and CVL laser scatter. A set of experiments were performed that verified that the detected LIF signal was linearly dependent on both the probe laser pulse energy and the NO₂ number density. Using the CVL, a LIF detection sensitivity of approximately 3×10^9 NO₂ cm⁻³ was achieved with signal averaging of 2.5×10^4 CVL pulses ($\approx 1-2$ s total time). Because of its higher pulse energy, the Nd: YAG probe provided



FIG. 1. Schematic of the experimental apparatus.

a single pulse sensitivity to NO_2 over ten times greater than the CVL. However, the sensitivity of the CVL system per unit time is much greater than the Nd:YAG scheme because of its higher average power.

8042

The timing and synchronization of the two lasers were controlled by a master clock (6–20 kHz), a frequency divider circuit, and two delay generators. The master clock pulses were used to trigger the CVL and the appropriately delayed low frequency (20–30 Hz) outputs of the frequency divider were used to trigger the excimer and the MCS data collection. This arrangement allowed for selection of a wide range of delay times between the excimer laser pulse, the copper vapor laser pulse, and the signal collection.

One unique advantage of the current design was related to the employment of a CVL as the probe laser. Because of its high repetition frequency, the CVL sampled the reactor contents every 50–150 μ s. Consequently, the temporal evolution of photolytic products from each excimer pulse could be monitored in real time long enough and with sufficient temporal resolution to characterize both the photodissociation yield and molecular diffusion out of the viewing zone. This information aided in determining the background probe signal and in ensuring that the photolytic products have completely left the viewing zone before the next excimer pulse. The large data return eliminated the need to systematically vary the triggering delays between the pump and the probe lasers for most experiments.

RESULTS AND DISCUSSION

Miller *et al.*³¹ have deduced that the majority of NO₂ produced from 248 nm photolysis of HNO₃ is initially in the ${}^{2}B_{2}$ state. We have verified their conclusion by quantitatively detecting the spontaneous visible emission that accompanies HNO₃ photolysis. The intensity and frequency range of the observed excimer induced fluorescence (EIF) is qualitatively similar to that observed by Oh *et al.*³⁰ and Miller *et al.*³¹ and attributed by them to emission from NO₂^{*}. From our experimental observations of the EIF we have estimated that the quantum yield for NO₂^{*} production from 248 nm photolysis of HNO₃ is greater than 0.6.

The temporal duration of the EIF was found to be less than 5 μ s (one channel width of the multichannel scaler) at all experimental pressures (1–10 Torr). This observed upper limit is consistent with the collisional lifetime that we calculate based on published values of the collision-free NO₂^{*} lifetime (~50 μ s) and collisional quenching constants (~6×10⁵ Torr⁻¹ s⁻¹ in Ar). The relatively short observed EIF lifetime reflects the fact that, under the present experimental conditions, relaxation of NO_2^* occurs predominately by stepwise collisional quenching rather than radiative decay.

The time scale for the establishment of the initial distribution of NO_2^{\dagger} is the same as for the decay of the EIF, i.e., less than 5 μ s following the photolysis pulse. The energy distribution of the NO_2^{\dagger} after a few microseconds is relatively narrow, consisting of a few highly excited vibrational levels near the 2B_2 threshold. This conclusion holds regardless of the nascent energy distribution of the NO_2^{\ast} produced from HNO₃ photolysis since the collisional quenching rates for 2B_2 NO₂ are orders of magnitude larger than for 2A_1 NO₂.

Detection of the photolytically generated NO₂[†] by LIF can begin only when the sum of the probe laser energy and the NO₂ internal energy is less than the NO₂ dissociation energy of 25 100 cm⁻¹. Consequently, fluorescence induced from the 511 nm (19 600 cm^{-1}) probe occurs only when the NO_2 internal energy is less than 5500 cm⁻¹. In order to properly interpret the observed NO2 LIF it was necessary to characterize the dependence of LIF sensitivity on NO2 internal energy for energies below 5500 cm^{-1} . The diffuseness of the visible NO₂ absorption spectrum suggests, in accordance with the Franck-Condon principle, that the overlap between the ${}^{2}B_{2}$ and ${}^{2}A_{1}$ states is a slowly varying function of vibrational level. A quantitative estimate of the Franck-Condon overlap integrals between these electronic levels of NO₂ was made using the model of Rosenstock and Sharp³² and the associated computer code of Yamaguchi et al.³³ For 511 nm probe excitation, the overlap integrals were nearly identical for both vibrationally cold NO2 and NO2 with up to two quanta of vibrational energy in any of the three modes. The calculation was limited to two vibrational quanta by computer code restrictions, nevertheless, the analysis strongly suggests that, provided the total energy is not beyond the thermochemical threshold for the dissociation of NO₂, the LIF signal will be relatively independent of the degree of vibrational excitation of the NO2. Accordingly, the LIF technique is uniformly sensitive to all ground state NO2 molecules with less than 5500 cm^{-1} of internal energy and is insensitive to NO₂ above that energy level. Figure 2 illustrates the relationship between the relaxation of NO₂ and the appropriate regions where the relaxation is being followed.

 NO_2 fluorescence data was collected under a range of pressures from 1–10 Torr and for a variety of different buffer gases. The temporal behavior of the observed LIF could be analyzed in terms of the following three processes: (1) an initial LIF signal that was due to nascent NO_2 with internal energies less than 5500 cm⁻¹; (2) a source of LIF signal that was due to relaxation of NO_2^{\dagger} from levels above 5500 cm⁻¹ of internal energy to levels below 5500 cm⁻¹; (3) a decay of the LIF signal that was due to the loss of NO_2 from the viewing zone because of diffusion, bulk gas flow, and secondary chemistry.

Analysis of low pressure data revealed that the amount of directly produced NO₂ with energy less than 5500 cm⁻¹ is small. This finding is consistent with other studies where the nascent NO₂ population from HNO₃ photolysis was measured.³¹ Consequently, process (1) was neglected as a source of LIF signal. The loss of NO₂ from the viewing zone [process (3)], was characterized by analysis of LIF data taken



FIG. 2. Relationship between the observed LIF signal and relaxation of NO₂. The nascent NO₂ distribution resulting from the photolysis of HNO₃ ranges from 12 000 cm⁻¹ to the total available energy of 23 700 cm⁻¹. Collisional quenching of NO₂ electronic energy is rapid and occurs prior to the commencement of LIF measurements. As a result the NO₂ population distribution at the start of LIF measurements is concentrated near the ²B₂ threshold energy (9500 cm⁻¹). No LIF signal is observed from NO₂ with internal energy above 5500 cm⁻¹ because the probe laser induces dissociation rather than fluorescence. Below 5500 cm⁻¹ of internal energy the Franck-Condon factors for NO₂ absorption of a probe laser photon are approximately equal. Accordingly, the temporal delay in the observation of LIF following HNO₃ photolysis can be related to the kinetic parameters associated with vibrational deactivation of highly excited (5500 cm⁻¹ <*E*_{int}<9500 cm⁻¹) ground state NO₂.

at higher buffer gas pressures. Under these pressure conditions the vibrational relaxation process, which produces the LIF signal, was complete before LIF data was recorded, i.e., $t>10 \ \mu$ s. Accordingly, the temporal behavior of the LIF after the first probe laser shot was dictated solely by process (3). The observed loss of NO₂ was well described by the following equation:

$$[\mathrm{NO}_2(t)] = A e^{-k_{\mathrm{loss}}t},\tag{2}$$

where $[NO_2(t)]$ is the NO₂ concentration and k_{loss} is a rate describing the loss of NO₂ from the viewing zone due to diffusion, gas flow, and secondary chemical removal. This expression has been applied successfully to a number of photolytically generated radicals and molecules.³⁴ In the present experiments the complete temporal evolution of the LIF signals were well described by Eq. (2) for every buffer gas employed when the total pressure was greater than 6 Torr.



FIG. 3. Temporal dependence of NO₂ LIF signal in two different buffer gases. The total pressure is 2 Torr and the concentration of HNO₃ is 1.6×10^{14} molecule cm⁻³. The filled circles are data taken in O₂ and the fit to the data is from Eq. (2) with $k_{loss}=1560 \text{ s}^{-1}$. The open circles correspond to Ar and the fit is to a 5 level kinetic model [Eq. (4)] with $k_{loss}=1520 \text{ s}^{-1}$ and $k_a=5.3 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹.

Measured loss rates were less than 500 s⁻¹ and were, as expected for diffusion controlled processes, inversely dependent on the total pressure.

At lower total pressures, the production of LIF signal due to relaxation of NO_2^+ [process (2)] became observable. The maximum observable rate of LIF growth, as defined by the detection electronics, was on the order of 10^5 s^{-1} . The rate of signal growth was readily observed to depend on the buffer gas (see Fig. 3). This latter observation supports the assumption that the LIF production is related to a vibrational quenching mechanism rather than some alternative explanation such as secondary chemical production of NO_2 .

Three kinetic models were applied to the experimental LIF data in order to estimate the quenching rate of the generated NO_2^{\dagger} . The simplest approach employed resembles the more detailed method of Donnelly *et al.*³ which was used to explain the collisional quenching from the 2B_2 levels of NO₂. The treatment consists of a manifold of *n* equally spaced levels with equivalent quenching rate coefficients between the adjacent levels. All of the initially generated NO₂ is assumed to be populated in one level which relaxes stepwise to the ground state. The model is fit to the data by varying the number of levels and the magnitude of the quenching rate coefficient. The solution is given by

$$\operatorname{LIF}(t) = \operatorname{LIF}(0) \left(1 - e^{-k_q t} \sum_{j=0}^{n-2} \frac{(k_q t)^j}{j!} \right), \qquad (3)$$

where k_q is the first order relaxation rate coefficient and LIF(t) is the fluorescence signal arising from NO₂ with internal energy less than 5500 cm⁻¹. In order to account for the loss of the NO₂, the product of Eqs. (2) and (3) was applied to the data, i.e.,

$$\mathrm{LIF}(t) = \mathrm{LIF}(0) \left(1 - e^{-k_q t} \sum_{j=0}^{n-2} \frac{(k_q t)^j}{j!} \right) e^{-k_{\mathrm{loss}} t}.$$
 (4)



FIG. 4. Temporal profile of NO₂ LIF signal in Ar. Total pressure is 1.5 Torr and the HNO₃ concentration is 7.7×10^{13} molecule cm⁻³. The dashed, solid, and dotted lines represent fits of Eq. (3) to the data with 2, 5, and 10 levels, respectively. The diffusional loss parameter, k_{loss} , is fixed at 2100 s⁻¹ and the rate coefficients in order of increasing number of levels are 3.7, 6.6, and 14.4×10^{-13} cm³ molecule⁻¹ s⁻¹.

The other kinetic models that were applied to the data are due to Adler–Golden,⁴ and Schwartz, Slawsky, and Herzfeld (SSH).¹⁸ The Adler–Golden model incorporates a quadratic (second order) dependence of the quenching rate coefficient on the excess energy of the NO₂, whereas the model developed from SSH theory incorporates a linear (first order) dependence of the rate coefficient on the excess energy. Since the model developed above has no energy dependence in the rate coefficients (zero order), a comparison of all three models to the data lends further insight into the actual energy dependence of the relaxation through these high lying vibrational states.

Figure 4 shows the temporal profile of the LIF signal following HNO₃ photolysis in an Ar buffer at a total pressure of 1.5 Torr. The values of k_q and k_{loss} were determined as a function of total number of levels by fitting the entire temporal profile (25 to 1000 μ s) to Eq. (4). The derived value of k_{loss} was independent of both the number of levels employed and k_q . Because the total quenching rates, i.e., k_qM , were, under all conditions, 1 to 2 orders of magnitude faster than k_{loss} , these two parameters were numerically uncoupled in the fitting routine.

The simple "zero order" model fit to the data is shown in Fig. 4. The fit improves as the number of levels are increased from 2 to 5, but degrades when more than 6 levels are incorporated. Adding more levels to the model effectively delays the initial growth of the signal because the system is relaxing through more states before reaching the lower vibrational levels where the LIF is observed. The inclusion of additional levels is accompanied by slightly larger calculated rate coefficients. Model fits were optimized for a number of data sets obtained under a range of experimental conditions. The number of vibrational levels required in the fits varied between 4 and 6. For comparison, the number of NO₂ vibrational levels that are contained within the experimen-



FIG. 5. The first order NO₂ vibrational quenching rates as a function of Ar pressure. The fractional concentration of HNO₃ in these runs is fixed at 2500 ppm. Each rate is determined from a fit of Eq. (4), where n=5, to temporal profiles of NO₂ LIF, as shown in Fig. 2. The solid line is a linear least square fit of the data. The slope of the line corresponds to a bimolecular quenching rate coefficient of $(4.5\pm0.4)\times10^{-13}$ cm³ molecule⁻¹ s⁻¹.

tally defined 4000 cm⁻¹ energy window (9500 to 5500 cm⁻¹) are 3, 5, and 2 for the ν_1 (1318 cm⁻¹), ν_2 (749.65 cm⁻¹), and ν_3 (1617.8 cm⁻¹) manifolds, respectively.⁵ This comparison suggests that the vibrational relaxation occurs via the manifold with the highest density of levels (i.e., ν_2). This proposed mechanism is consistent with predictions based on energy gap models.

The application of the "first order" SSH model to the data resulted in rate coefficients that are virtually identical to those derived from the "zero order" model fit. This agreement reflects the approximate constancy of rate coefficients predicted by SSH theory for high vibrational quantum numbers. The application of the "second order" Adler-Golden model to the data resulted in significantly worse fits compared to the other two. Upon analysis of these fits it was clear that the quadratic rate coefficient dependence on vibrational level is too strong to properly mimic the experimental observations.

The first order relaxation rates derived from the zero order model are linear with pressure as shown in Fig. 5. The slope of the fitted line gives a value of $(4.5\pm0.4)\times10^{-13}$ cm³ molecule⁻¹ s⁻¹ for the bimolecular quenching rate coefficient in Ar, where the quoted error is at the $\pm 1\sigma$ precision

limit. An average of data acquired at different total pressures yields a quenching rate coefficient of $(5.1\pm0.5)\times10^{-13}$ cm³ molecule⁻¹ s⁻¹ for relaxation in Ar. All of the other carrier gases were found to be more efficient than Ar in relaxing the NO₂ through the high vibrational states. The results are summarized in Table I along with previous literature results.

The absolute rate coefficients obtained in the present study are larger than the previously reported values. Reference 14 and 16 reported the slowest relaxation rates. The absolute rate coefficient from Ref. 14 is an estimate based on a comparison to other data and no uncertainty on this value was presented. The relaxation rate in Ref. 16 represents deactivation of NO₂(010), i.e., $E_{int}=750 \text{ cm}^{-1}$. The results of Ref. 15, in which relaxation was monitored through the entire vibrational manifold, i.e., $E_{int} \leq 9500 \text{ cm}^{-1}$, are intermediate between the present values and those of Ref. 16. The present rate coefficients, which correspond to relaxation solely in the region of 5500 cm⁻¹ $\leq E_{int} \leq 9500 \text{ cm}^{-1}$, continue a trend which can be rationalized in terms of a dependence of the rate coefficient on total internal energy.

The relative rate coefficients agree well with literature values. The relative rates in Ar, N_2 , and O_2 are, within the stated error, identical to those reported in Ref. 14. The ratio of the rates in CO_2 and He from Ref. 15 are within a factor of 2 of the present results and overlap one another within the cited precision.

CONCLUSION

The majority of NO₂ generated from photolysis of HNO₃ at 248 nm is electronically excited. The nascent NO_2^* is rapidly redistributed by collisional deactivation into a relatively narrow energy region near the threshold of the 2B_2 manifold near 9500 cm⁻¹. Quenching rate coefficients for relaxation through the higher vibrational levels of the 2A_1 manifold were determined by a fit of LIF data to a simple stepwise kinetic mechanism. The model fits indicate that approximately 4 to 6 vibrational levels are involved in the deactivation of the NO₂ from a narrow distribution centered at 9500 cm⁻¹ to levels below 5500 cm⁻¹. This finding suggests that the relaxation process occurs primarily through the ν_2 manifold. The measured vibrational relaxation rates were found to depend strongly on the collision partner. The derived rate coefficients are larger than in those studies where relaxation

TABLE I. Summary of experimental relaxation rate coefficients for NO₂⁺.

| М | $k(10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ | | | | k/k _{Ar} | |
|-----------------|---|-----------------|-----------|----------------|-------------------|---------------|
| | Ref. 14 | Ref. 15 | Ref. 16 | This work | Ref. 14 | This work |
| Ar | 0.6ª | | 0.51±0.10 | 5.1±0.5 | 1.0 | 1.0 |
| He | | 1.8 ± 0.6 | | 10.0 ± 1.0 | | 2.0 ± 0.3 |
| Xe | | 3.3 ± 0.9 | | | | |
| N_2 | | | | 14.0 ± 2.0 | 2.0 ± 0.5 | 2.7 ± 0.2 |
| O_2 | | | | 26.0 ± 6.0 | 5.0 ± 2.0 | 5.0 ± 1.0 |
| CO ₂ | | 27.0 ± 12.0 | | 87.0±11.0 | | 17.0±3.0 |
| NO | | | | | 40.0±25.0 | |
| NO_2 | | 33.0±12.0 | | | 55.0±35.0 | |

^aEstimate only.

through lower vibrational states was probed. These results are consistent with theories that predict a dependence of the vibrational relaxation rate on total internal energy.

ACKNOWLEDGMENTS

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract to the National Aeronautics and Space Administration. We thank David P. Natzic for assistance in the design and construction of the experimental apparatus.

- 1 K. Uehara and H. Sasada, High Resolution Spectral Atlas of NO₂ 559–597 nm (Springer, New York, 1985).
- ²A. Weaver, R. B. Metz, S. E. Bradforth, and D. M. Neumark, J. Chem. Phys. **90**, 2070 (1989).
- ³V. M. Donnelly, D. G. Keil, and F. Kaufman, J. Chem. Phys. **71**, 659 (1979).
- ⁴S. M. Adler-Golden, J. Phys. Chem. 93, 684 (1989).
- ⁵H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).
- ⁶A. E. Douglas, J. Chem. Phys. **45**, 1007 (1966).
- ⁷K. Sakurai and H. P. Broida, J. Chem. Phys. 50, 2404 (1969).
- ⁸S. E. Schwartz and H. S. Johnston, J. Chem. Phys. 51, 1286 (1969).
- ⁹V. M. Donnelly and F. Kaufman, J. Chem. Phys. 66, 4100 (1977).
- ¹⁰ V. M. Donnelly and F. Kaufman, J. Chem. Phys. 69, 1456 (1978).
- ¹¹C. H. Chen, S. D. Kramer, D. W. Clark, and M. G. Payne, Chem. Phys. Lett. **65**, 419 (1979).
- ¹²O. Cheshnovsky and A. Amirav, Chem. Phys. Lett. 109, 368 (1984).
- ¹³C. Anastasi and D. U. Hancock, J. Chem. Soc., Faraday Trans. 2 84, 1697 (1988).

- ¹⁴M. F. Golde and F. Kaufman, Chem. Phys. Lett. 29, 480 (1974).
- ¹⁵ J. J. F. McAndrew, J. M. Preses, R. E. Watson, Jr., and G. W. Flynn, J. Chem. Phys. **90**, 4772 (1989).
- ¹⁶B. M. Toselli, T. L. Walunas, and J. R. Barker, J. Chem. Phys. **92**, 4793 (1990).
- ¹⁷J. L. Hardwick, J. Mol. Spectrosc. 109, 85 (1985).
- ¹⁸R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, J. Chem. Phys. 20, 1591 (1952).
- ¹⁹A. A. Turnipseed, G. L. Vaghjiani, J. E. Thompson, and A. R. Ravishankara, J. Chem. Phys. **96**, 5887 (1992).
- ²⁰ T. Berces and S. Forgeteg, Trans. Faraday Soc. 66, 633 (1970).
- ²¹H. S. Johnston, S.-G. Chang, and G. Whitten, J. Phys. Chem. 78, 1 (1974).
- ²²H. Okabe, J. Chem. Phys. 72, 6642 (1980).
- ²³M. Suto and L. C. Lee, J. Chem. Phys. 81, 1294 (1984).
- ²⁴G. S. Jolly, D. L. Singleton, D. J. McKenney, and G. Paraskevopoulos, J. Chem. Phys. 84, 6662 (1986).
- ²⁵R. D. Kenner, F. Rohrer, Th. Papenbrock, and F. Stuhl, J. Phys. Chem. 90, 1294 (1986).
- ²⁶ A. Jacobs, K. Kleinermanns, H. Kuge, and J. Wolfrum, J. Chem. Phys. 79, 3162 (1983).
- ²⁷J. Schlutter and K. Kleinermanns, Chem. Phys. Lett. 192, 94 (1992).
- ²⁸ M. D. Likar, A. Sinha, T. M. Ticich, R. L. Vander Wal, and F. F. Crim, Ber. Bunseges Phys. Chem. 92, 289 (1988).
- ²⁹ J. August, M. Brouard, M. P. Docker, A. Hodgson, C. J. Milne, and J. P. Simons, Ber. Bunseges Phys. Chem. **92**, 264 (1988).
- ³⁰D. Oh, W. Sisk, A. Young, and H. Johnston J. Chem. Phys. 85, 7146 (1986).
- ³¹C. E. Miller, Ph.D. dissertation, University of California, Berkeley (1991).
- ³²T. E. Sharp and H. M. Rosenstock, J. Chem. Phys. 41, 3453 (1964).
- ³³M. Yamaguchi, T. Momose, and T. Shida, J. Chem. Phys. 93, 4211 (1990).
- ³⁴H. H. Nelson and H. S. Johnston, J. Phys. Chem. 85, 3891 (1981).
- ³⁵T. Shimanouchi, J. Phys. Chem. Ref. Data 6, 993, (1977).