

Collisional electronic quenching rates for NO $A^2\Sigma^+(v' = 0)$

P.H. Paul^a, J.A. Gray^{a,1}, J.L. Durant Jr.^a, J.W. Thoman Jr.^b

^a Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94550, USA

^b Department of Chemistry, Williams College, Williamstown, MA 01267, USA

Received 13 February 1996; in final form 10 June 1996

Abstract

We report rate coefficients for electronic quenching of NO $A^2\Sigma^+(v' = 0)$ by CO, CO₂, H₂, H₂O, O₂, NO, N₂O, NO₂, and Ar measured at room temperature and at elevated temperatures behind reproducible shocks. The magnitudes of the rates and the observed temperature dependencies of NO $A^2\Sigma^+$ quenching by these collision partners are found to be in accord with a charge-transfer (harpoon) collision model for the process.

1. Introduction

Nitric oxide (NO) is an important combustion-generated pollutant [1,2], is a common component in supersonic flows, and is often used as a tracer for laser-induced fluorescence (LIF) flowfield diagnostics [3]. In order to make NO LIF measurements quantitative, however, a detailed knowledge of the collisional electronic quenching of NO by other species over a wide range of temperatures is required.

The rate coefficients for quenching of NO $A^2\Sigma^+$ by many species have been measured in flames [4–6], in flow cells [7–14], and in shock tubes [15–18]. We have previously reported measurements for electronic quenching and VET in NO $A^2\Sigma^+$ by N₂ [17], and for electronic quenching in NO $A^2\Sigma^+$, by CO₂ and NO [16], and by a variety of hydrocar-

bons and ammonia [18]. Here we report rate coefficients for electronics quenching of NO $A^2\Sigma^+(v' = 0)$ by CO, CO₂, H₂, H₂O, O₂, NO, N₂O, NO₂ and Ar measured in the range of 300 to 4500 K. The data are compared to previously reported values for the quenching rate. We also compare the measurements to the trends predicted by an ion-pair intermediate (harpoon) model for the process.

2. Experiment

The shock tube and the probe laser systems have been described previously [19,16]. Piezoelectric pressure transducers, used to measure the shock speed, trigger a single laser pulse which is directed axially down the center of the shock tube. The laser is tuned to 44337.7 cm⁻¹ (approximately 1 mJ, 6 ns, 0.25 cm⁻¹) to excite the NO $A^2\Sigma^+ \leftarrow X^2\Pi(0,0) R_1(17)$ transition. Laser-induced fluorescence is collected through a bandpass filter (260 ± 5 nm) onto a photomultiplier tube. The bandpass filter selects fluorescence from the NO $A \rightarrow X(0,3)$ band in order to

¹ Present address: Dept. of Chemistry, Ohio Northern Univ. Ada, OH 45810, USA.

avoid any problem with radiation trapping. The photomultiplier is wired to use a limited number of dynodes to optimize dynamic range. The signal was pre-amplified ($10 \times$ gain) and recorded by a digital oscilloscope (LeCroy 9450A). Dispersed fluorescence spectra, measured with a time-gated optical multichannel analyzer, indicated that rotational thermalization occurs on the timescale of the experiment, thus quenching may occur from a number of rotational states. The observed rotational thermalization is consistent with argon being the predominant collision partner in the test gas and a rate coefficient for rotational energy transfer in the NO A-state by argon of order $9.3 \times 10^{-11} \text{ cm}^3/\text{s}$ [20].

Gas mixtures are prepared in a Teflon-lined vessel by measuring the partial pressures of the various gas components with a capacitance manometer (MKS Baratron). After preparation and prior to use, the gas mixtures were allowed to stand for at least 15 h to ensure thorough mixing. Before each run the driven section of the shock tube was evacuated to $\leq 7 \times 10^{-5}$ mbar, the test gases were then allowed to flow through the driven section of the shock tube for at least five minutes. This ensures passivation of the walls of the shock tube and thus a reliable composition of the test mixture.

In the experiments designed to measure quenching by water the test gas was produced by adding a premix of argon seeded with a trace of NO in argon that has been bubbled through distilled water. The argon was introduced into the water through a glass frit. The concentration of the water vapor in the argon was fixed by the temperature of the system. To minimize the loss of water to condensation, the liquid water was maintained at less than room temperature by suspending the container in a temperature controlled bath (NESLAB) and the resulting mixture was allowed to rise to room temperature by passage through a coil of copper tubing. The argon–NO premix was then added and the gases were allowed to flow through a column packed with gas beads to ensure thorough mixing. The flow rates of the argon feeding the water bath and of the argon–NO premix were measured with calibrated mass-flow meters (MKS Baratron). Again, the test gases were allowed to flow through the driven section of the shock tube for a period of time to ensure passivation and a stable composition.

For the room temperature measurements the shock tube is used as a simple pressure vessel. In this configuration decay traces were obtained over a range of static pressures. For intermediate range temperatures (900 to 2300 K) an incident shock geometry was employed. For the high range temperatures (2300 to 4500 K) the facility was reconfigured with a longer driver section and reflected shocks were used. For this later configuration the signal was collected through a bandpass filter ($290 \pm 5 \text{ nm}$) to isolate fluorescence from the NO A \rightarrow X (0,5) system. Although this band is weaker than the (0,3) band, it was chosen because radiation trapping by the NO X² Π is a much more serious problem at the higher temperatures. For the high temperature runs the tube was evacuated to $\leq 7 \times 10^{-6}$ mbar to further reduce thermally induced background emission and quenching by impurities which are more serious problems under reflected shock conditions.

3. Results

Laser-induced fluorescence data from over 990 high-temperature shock-tube runs and more than 500 room-temperature runs are used in the data analysis. The fluorescence decay of each run is fit to the equation:

$$I(t) = I_0 \exp(-t/\tau_{\text{obs}}) + \text{baseline}, \quad (1)$$

where $I(t)$ is the fluorescence intensity observed at time t , I_0 is the fluorescence intensity at time zero, and τ_{obs} is the observed fluorescence lifetime. To avoid interference from the laser pulse when fitting the exponential decays, the first thirty nanoseconds (twelve data points) after the fluorescence intensity peak are not used. For each gas mixture and for each temperature, τ_{obs} is measured between five and twelve times and then averaged. Species-dependent quenching rate coefficients are then obtained from the relation

$$1/\tau_{\text{obs}} = \sum_x k_x [\text{X}] + 1/\tau_{\text{rad}}, \quad (2)$$

where k_x and $[\text{X}]$ are the quenching rate coefficient and the number density for species X, respectively. The radiative lifetime of NO A² Σ^+ ($v' = 0$) was taken to be $\tau_{\text{rad}} = 220 \text{ ns}$ [9,21]. The gas mixtures used in

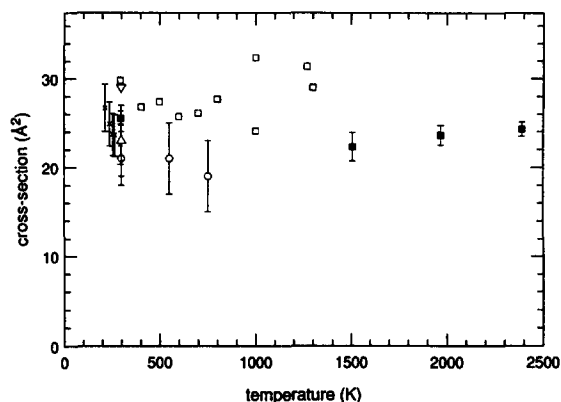


Fig. 1. Cross-section for collisional quenching of NO A $2\Sigma^+$ ($v' = 0$) by O₂. ■ this work, □ (Ref.[13]), ○ (Ref. [12]), × (Ref. [14]), △ (Ref.[10]), and ▽ (Ref. [11]).

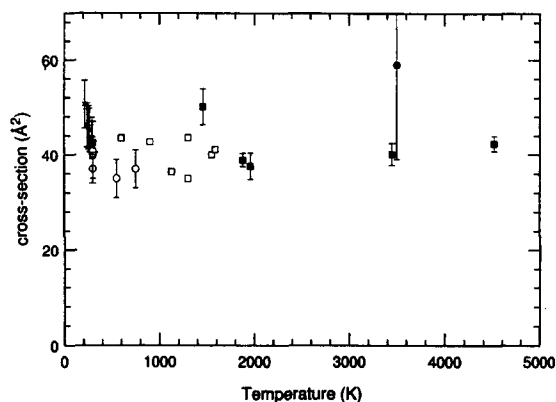


Fig. 2. Cross-section for collisional quenching of NO A $2\Sigma^+$ ($v' = 0$) by NO. Data labeled as in Fig. 1 and ● (Ref.[15]).

the experiments were designed so that one species dominates the quenching. However, the summation (implied sum over species in Eq. (2)) was extended to include all species with non-negligible concentrations.

The measured quenching rate coefficients are converted to an effective quenching cross-sections, σ'_x , by the relationship

$$\sigma'_x = k_x / \langle v \rangle, \quad (3)$$

Table 1
Observed rate coefficients for quenching of NO A $2\Sigma^+$ ($v' = 0$)

Species	T (K)	$k \times 10^{11}$ (cm ³ /s)	Species	T (K)	$k \times 10^{11}$ (cm ³ /s)
Ar	298	< 0.02	H ₂ O	298	89.7 (4.6)
	1880	< 0.018		1462	51.1 (4.5)
	3450	< 0.010		1901	51.3 (3.7)
	4515	< 0.021		2283	53.1 (3.2)
N ₂ O	298	50.6 (3.3)	O ₂	298	16.2 (0.5)
	1464	83.4 (7.8)		1506	32.0 (1.7)
	1906	97.8 (7.7)		1967	38.7 (1.7)
	2301	99.9 (4.2)		2391	43.9 (1.3)
NO ₂	298	53.6 (5.2)	H ₂	1880	1.0 (0.4)
	1464	109 (7.2)		2307	2.6 (0.2)
	1906	100 (9.3)	NO	298	27.4 (0.78)
CO	298	4.06 (0.05)		1458	71.8 (5.4)
	1449	12.1 (0.6)		1880	63.4 (2.3)
	1903	17.4 (0.7)		1960	62.5 (4.7)
	2310	22.3 (0.7)		3450	88.5 (5.0)
CO ₂	298	42.9(1.0)		4515	107.(4.0)
	1505	68.2 (5.0)			
	1948	84.9 (5.0)			
	2401	94.5 (5.0)			

Values in parentheses represent 2σ uncertainty.

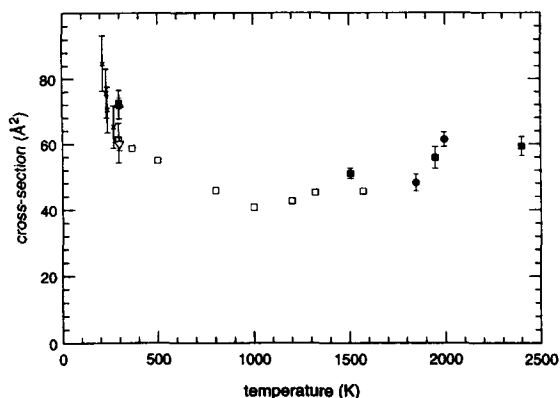


Fig. 3. Cross-section for collisional quenching of NO $A^2\Sigma^+$ ($v' = 0$) by CO_2 . Data labeled as in Fig. 1 except \bullet (Ref. [16]) and ∇ (Ref. [9]).

where the average collision velocity is given by

$$\langle v \rangle = (8kT/\pi\mu)^{1/2}. \quad (4)$$

Here k is the Boltzmann constant, T is the absolute temperature, and μ is the reduced mass of the collision pair. For the room temperature measurements, the fluorescence lifetime of each species was measured repeatedly over a range of five to ten different pressures, which typically varied over an order of magnitude. The quenching cross-sections were obtained by a least squares fit of these data to Eq. (2).

A summary of the observed quenching rate coefficients is given in Table 1. The cross-sections are shown plotted as functions of temperature in Figs.

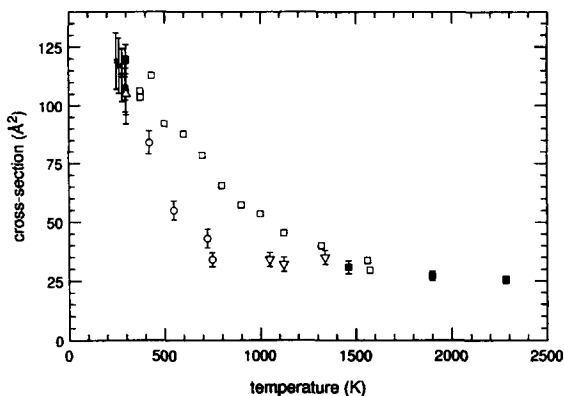


Fig. 4. Cross-section for collisional quenching of NO $A^2\Sigma^+$ ($v' = 0$) by H_2O . Data labeled as in Fig. 1 except ∇ (Ref. [4]).

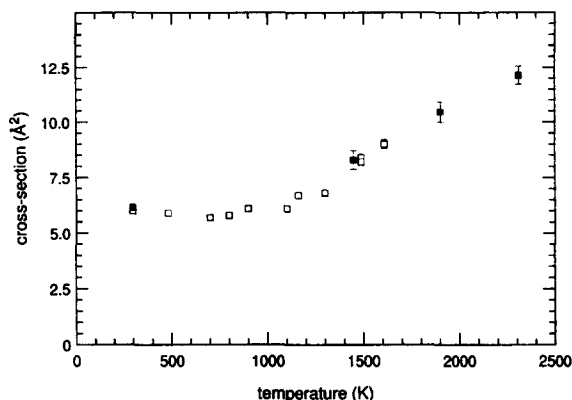


Fig. 5. Cross-section for collisional quenching of NO $A^2\Sigma^+$ ($v' = 0$) by CO. \blacksquare this work and \square (Ref. [13]).

1–5, along with the results of other workers. The data are quoted with estimates for the two-standard deviation statistical uncertainty in the measurements.

4. Discussion

The cross-section for quenching by Ar is found to be $< 0.01 \text{ Å}^2$ from 298 to 4520 K. This value is consistent with other measurements which place the value at 300 K at $< 0.007 \text{ Å}^2$ [10,13,20] and $< 0.002 \text{ Å}^2$ at 995 K [13]. The lighter noble gases appear to be very inefficient at quenching NO $A^2\Sigma^+$. For quenching by He cross-sections of 0.002 Å^2 at 300 K [13] and $< 0.005 \text{ Å}^2$ at 1848 K [16] have been reported. A value of $< 0.017 \text{ Å}^2$ [10] for quenching by Ne at 300 K has also been reported. Relatively small cross-sections of < 0.22 and $< 0.52 \text{ Å}^2$ are found for quenching by H_2 at 1880 and 2307 K, respectively. Drake and Ratcliff report values of 0.0019 and 0.0078 Å^2 for quenching by H_2 at 300 and 793 K, respectively [13].

The cross-section for quenching by O_2 and NO are of order 25 and 42 Å^2 , respectively, and appear to be independent of temperature (see Figs. 1 and 2). Below temperatures of 1200 K, the results reported here agree reasonably well with the measurements of Drake and Ratcliff [13] however they appear to be systematically larger than the measurements of Raiche and Crosley [12]. Meier et al. [15] report the only other high temperature measurement, to our knowledge, giving a value of $59 \pm 20 \text{ Å}^2$ for quench-

ing of $\text{NO } A^2\Sigma^+$ by NO at 3900 K. This value was determined from a single set of measurements using NO seeded in N_2 and performed in a shock tube experiment designed to simulate bow shocks of vehicles at high altitudes. As such their value for the NO quenching cross-section is very sensitive to the value they determined for the N_2 quenching cross-section. The present measurements, designed explicitly to measure quenching by NO by using a bath of Ar, yield the somewhat lower value of 41.5 \AA^2 at 3900 K as interpolated from the data.

The cross-section for quenching by NO_2 at 300 K was measured at $91.5 \pm 8.8 \text{ \AA}^2$ which is higher than the value of $63 \pm 3 \text{ \AA}^2$ reported by Assher and Haas [7]. With increasing temperature, the cross-section falls slightly to $83.4 \pm 5.5 \text{ \AA}^2$ at 1465 K and then more sharply to $67.3 \pm 6.2 \text{ \AA}^2$ at 1906 K.

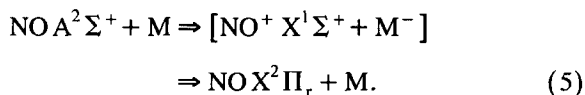
The cross-sections for quenching by N_2O and CO_2 both fall from values of 85.1 ± 11.2 and $72.5 \pm 3.2 \text{ \AA}^2$ at 300 K, respectively, to values of order 50 and 63 \AA^2 , respectively, which appear to be relatively temperature independent from 1200 to 2500 K (for CO_2 see Fig. 3). The present measurement for quenching by N_2O at 300 K is higher than the value of $63.5 \pm 8.2 \text{ \AA}^2$ reported by Greenblatt and Ravishankara [10]. Similarly the measurements for quenching by CO_2 from 300 to 1500 K are somewhat higher than the values reported by Drake and Ratcliff [13] but the measurements at 300 K agrees very well with the value of $72.1 \pm 4.4 \text{ \AA}^2$ reported by Greenblatt and Ravishankara [10].

A far more dramatic fall with increasing temperature is observed in quenching by H_2O in which case the cross-section drops from 110 to 28 \AA^2 in going from 300 to 1000 K. However the value becomes relatively temperature independent from 1000 to 2300 K (see Fig. 4). The present measurement of $119 \pm 6 \text{ \AA}^2$ for quenching by water at 300 K is about 10% higher than other reported values: $106 \pm 10 \text{ \AA}^2$ by Raiche and Crosley [12], $107.4 \pm 5 \text{ \AA}^2$ by Drake and Ratcliff [13], and $105 \pm 13 \text{ \AA}^2$ by Greenblatt and Ravishankara [10]. The systematic difference is ascribed to the difficulty in producing a mixture containing an accurately known quantity of water vapor. The tendency in such measurements is to systematically over-predict the amount of water vapor present in the test cell hence to measure a systematically smaller cross-section. The high temperature limiting

value appears in reasonable agreement with the values reported by Cattolica et al. [4] and by Drake and Ratcliff [13].

Fig. 5 shows the temperature dependence in the cross-section for quenching by CO. In this case the cross-section is near 6 \AA^2 at room temperature and appear to rise continuously for temperature from 1400 to 2300 K. The present measurements are in excellent agreement with the results of Drake and Ratcliff [13].

The magnitude of the cross-section for quenching $\text{NO } A^2\Sigma^+$ exhibits a strong dependence on collision partner and displays a variety of behaviors with temperature. Haas and coworkers [7,11] have proposed that quenching in $\text{NO } A^2\Sigma^+$ by the collision partner M follows a classic 'harpoon' mechanism, i.e.



According to this model, the entrance channel for quenching occurs at an intersection between the covalent excited state surface and the ionic pair surface. For collision partners having highly unstable negative ions (e.g. H_2 with an adiabatic electron affinity of order -3 eV) access to this intersection is energetically precluded in a thermal collision. From this standpoint the model reliably predicts collision partners that are observed to be relatively inefficient at quenching $\text{NO } A^2\Sigma^+$. The model is in good agreement with the observations of very small cross-sections for quenching by He [16,20], Ne [10], Ar, H_2 , CF_4 and SiF_4 [11] as well as CH_4 , C_2H_6 , and C_3H_8 [18].

Recently we have reported the results of an extensive test of the harpoon model [22]. We have enlarged the calculation employed by Haas and coworkers [7,11] to include more complete potentials for the neutrals and the ions, albeit multipole expansions, and have employed a Landau–Zener formalism for the probability of 'crossing' at the surface intersections. Following Gislason and Sachs [23], the matrix element of the perturbation potential that mixes the zeroth order states was taken as the product of an electronic wave function (in the form of the Hasted–Chong correlation as parameterized by Olsen et al.[24]) with the vibrational overlaps in the form of

electron donor and electron acceptor Franck–Condon factors. Following Bauer et al. [25] we have employed a 'unit-flux' algorithm which considers the full set of possible entrance channels defined by the energetically accessible vibrational levels in the neutrals and the ions. In the calculation we have also included provision for the action of an orbiting collision. A value of 1.1 D was used for the dipole moment of $\text{NO } A^2\Sigma^+$ [26]. While being relatively simple this model performs well at predicting the observed behavior in the variation in the quenching cross-section with collision partner and with temperature [22]. For example, the calculation suggests that the outermost entrance channel is sufficiently attractive in collisions with molecules like NO and O_2 , that the cross-sections should be of order gas kinetic and should be relatively weak functions of temperature for $T > 250$ K which is in good agreement with the data.

In our previous work we have reported that energy-barrier like behavior is observed in quenching of $\text{NO } A^2\Sigma^+$ by N_2 [17]. The adiabatic affinity of N_2 is of order -1.9 eV [27] in which case the outermost entrance channel is predicted to be on the repulsive wall of the covalent potential. A similar behavior is seen here in quenching of $\text{NO } A^2\Sigma^+$ by CO at higher temperatures. The adiabatic affinity of CO is of order -1.4 eV [28], thus we expect a behavior like that seen in quenching by N_2 . However, between 300 and 1000 K the cross-section for quenching by CO appears to be relatively constant at a value of order 6 \AA^2 . One possible explanation for the low temperature behavior is near-resonant $E \rightarrow V$ transfer which could operate for CO (owing to the presence of bound vibrational levels in $\text{CO } X^1\Sigma^+$ at over 5.5 eV and to a dipole moment of order 0.1 D). Such a process has been observed for quenching of $\text{O}(^1\text{D})$ by CO [29]. Using the several procedures outlined by Breckenridge et al. [30] we estimate a cross-section of 5 \AA^2 for quenching of $\text{NO } A^2\Sigma^+$ by CO at 300 K. This cross-section should fall with increasing temperature, functionally between $\sigma \propto T^{-1}$ to $\ln \sigma \propto T^{-1/3}$. Thus the combined behavior of the $E \rightarrow V$ mechanism predominating at low temperatures and the predicted energy barrier-like behavior of the harpoon mechanism predominating at higher temperatures appear consistent with the experimental data.

5. Conclusions

We have reported rate coefficients for electronic quenching of $\text{NO } A^2\Sigma^+(v' = 0)$ by CO, CO_2 , H_2 , H_2O , O_2 , NO, N_2O , NO_2 , and Ar measured at room temperature and at elevated temperatures behind reproducible shocks. Cross-sections for quenching by Ar and H_2 were found to be relatively small. Whereas the cross-sections for the other species studied were found to be of order gas kinetic. At temperatures below 1000 K the measurements were found to be in reasonably good agreement with previously published values. The magnitude of the rates and the observed temperature dependence of $\text{NO } A^2\Sigma^+$ quenching by these collision partners appears to be consistent with a charge-transfer (harpoon) collision model. The measurements above 1000 K enlarge the existing experimental data base for quenching of $\text{NO } A^2\Sigma^+(v' = 0)$ and should be particularly useful in the development of quantitative laser-induced fluorescence diagnostic techniques for combustion and aerothermodynamic applications.

Acknowledgements

The authors would like to thank Mr. G.B. Sartor for his expert technical assistance in the laboratory. This work was supported by The United States Department of Energy, Office of Basic Energy Sciences, Chemical Science Division. JWT acknowledges the support of Associated Western Universities for an AWU-DOE faculty sabbatical fellowship.

References

- [1] J.A. Miller and C.T. Bowman, *Prog. Energy Combust. Sci.* 15 (1989) 287.
- [2] L.R. Thorne, M.C. Branch, D.W. Chandler, R.J. Kee and J.A. Miller, *The 23rd symposium (international) on combustion* (The Combustion Institute, Pittsburg, PA, 1990), pp. 965.
- [3] R.K. Hanson, J.M. Seitzman and P.H. Paul, *Appl. Phys. B* 50 (1990) 441.
- [4] R.J. Cattolica, T.G. Mataga and J.A. Cavolowsky, *J. Quant. Spectrosc. Radiat. Transfer* 42 (1989) 499.
- [5] D.E. Heard, J.B. Jeffries and D.R. Crosley, *Chem. Phys. Lett.* 178 (1991) 533.

- [6] R. Schwarzwald, P. Monkhouse and J. Wolfrum, *Chem. Phys. Lett.* 158 (1989) 60.
- [7] M. Assher and Y. Haas, *J. Chem. Phys.* 76 (1982) 2115; Y. Haas and M. Assher, *Adv. Chem. Phys.* 47 (1981) 17.
- [8] H. Zacharis, J.B. Halpern and K.H. Welge, *Chem. Phys. Lett.* 43 (1976) 41.
- [9] I.S. McDermid and J.B. Laudenslager, *J. Quant. Spectrosc. Radiat. Transfer* 27 (1982) 483.
- [10] G.D. Greenblatt and A.R. Ravishankara, *Chem. Phys. Lett.* 136 (1987) 501.
- [11] Y. Haas and G.D. Greenblatt, *J. Phys. Chem.* 90 (1986) 513.
- [12] G.A. Raiche and D.R. Crosley, *J. Chem. Phys.* 92 (1990) 5211.
- [13] M.C. Drake and J.W. Ratcliffe, *J. Chem. Phys.* 98 (1993) 3850.
- [14] R. Zhang and D.R. Crosley, *J. Chem. Phys.* 102 (1995) 7418.
- [15] U.E. Meier, G.A. Raiche, D.R. Crosley, G.P. Smith and D.J. Eckstrom, *Appl. Phys. B* 53 (1991) 138.
- [16] J.A. Gray, P.H. Paul and J.L. Durant, *Chem. Phys. Lett.* 190 (1992) 266.
- [17] J.W. Thoman Jr., J.A. Gray, J.L. Durant Jr. and P.H. Paul, *J. Chem. Phys.* 97 (1992) 8156.
- [18] M.R. Furlanetto, J.W. Thoman Jr., J.A. Gray, P.H. Paul and J.L. Durant Jr., *J. Chem. Phys.* 101 (1994) 10452.
- [19] J.A. Gray, *Rev. Sci. Instrum.* 61 (1990) 1825.
- [20] H.P. Broida and T. Carrington, *J. Chem. Phys.* 38 (1963) 136.
- [21] A.J. Smith and F.H. Read, *J. Phys. B* 18 (1978) 3263.
- [22] P.H. Paul, J.A. Gray, J.L. Durant Jr. and J.W. Thoman Jr., *Appl. Phys. B* 57 (1993) 249.
- [23] E.A. Gislason and J.G. Sachs, *J. Chem. Phys.* 62 (1975) 2678.
- [24] R.E. Olsen, F.T. Smith and E. Bauer, *Appl. Opt.* 10 (1971) 1848.
- [25] E. Bauer, E.R. Fisher and F.R. Gillmore, *J. Chem. Phys.* 51 (1969) 4173.
- [26] J.A. Gray, R.L. Farrow, J.L. Durant and L.R. Thorne, *J. Chem. Phys.* 99 (1993) 4327.
- [27] A. Lofthus and P.H. Krupenic, *Phys. Chem.* 6 (1977) 113.
- [28] G.J. Schulz, *Phys. Rev. A* 135 (1964) 988.
- [29] G. Karl, P. Kruus and J.C. Polanyi, *J. Chem. Phys.* 46 (1967) 224.
- [30] W.H. Breckenridge, R.P. Blickensderfer, J. Fitzpatrick and D. Oba, *J. Chem. Phys.* 70 (1979) 4751.