PUBLISHED VERSION

http://hdl.handle.net/2440/862

Collisional deactivation of $N_2O(00^01)$ studied by time-resolved infrared fluorescence

Kathleen L. Poel, Zeyad T. Alwahabi, and Keith D. King
Department of Chemical Engineering, University of Adelaide, Australia 5005

The time-resolved infrared fluorescence (IRF) technique has been used to study the vibrational deactivation of excited N_2O by large polyatomic colliders at ambient temperature (295±2 K). $N_2O(00^01)$ molecules were prepared by direct pumping with the $P(18)$ line of a pulsed CO_2 laser at 9.536 μm. The bimolecular rate constant for self-deactivation was determined to be $(0.763\pm0.006)\times10^3$ Torr^{-1} s^{-1}, in very good agreement with previous work. The rate constants for deactivation by Ar and H_2 were found to be (0.103 ± 0.003) and $(4.89\pm0.52)\times10^3$ Torr^{-1} s^{-1}, respectively. The deactivation rate constants for the large polyatomic molecules, c-C_6H_{10}, c-C_6H_{12}, C_6H_6, C_6D_6, C_7H_8, C_7D_8, C_6H_5F, p-$C_6H_4F_2$, C_6HF_5 and C_6F_6, were found to be (176 ± 10), (153 ± 22), (115 ± 4), (201 ± 2), (127 ± 11), (407 ± 52), (144 ± 14), (173 ± 13), (129 ± 8), and $(48\pm9)\times10^3$ Torr^{-1} s^{-1}, respectively. Experimental deactivation probabilities and average energies removed per collision are calculated and compared. There is little difference in deactivation probabilities between the acyclic ring compounds and their aromatic analogues and the partially-fluorinated benzenes but the perfluorinated compound, C_6F_6 is much less efficient than the other species. The perdeuterated species, C_6D_6 and C_7D_8, especially the latter, show enhanced deactivation relative to the other species, probably as a result of near-resonant intermolecular $V-V$ energy transfer. The results are compared with our recent work on the deactivation of $CO_2(00^01)$ by the same group of large polyatomic colliders [K. L. Poel, Z. T. Alwahabi, and K. D. King, Chem. Phys. **201**, 263 (1995)]. © *1996 American Institute of Physics.* [S0021-9606(96)00825-2]

I. INTRODUCTION

Carbon dioxide and nitrous oxide are important prototype systems for understanding gas-phase energy transfer processes. They make an important comparative pair because they are isoelectronic, have the same mass, and have similar vibrational frequencies. Moreover while the change in average energy transfer over the range from low-lying vibrational levels to high vibrational energies (quasicontinuum) awaits full characterization, small molecules at low excitation energies provide a useful guide to understanding and predicting the energy transfer behavior of large molecules. CO_2 has long been used as an important prototype system but the studies of N_2O began much more recently and are far less extensive.

Excited N_2O [in the (00^01) vibrational level of the asymmetric stretch mode, ν_3] may be prepared either by direct laser excitation or by indirect collisional pumping from another laser-excited species, and then monitored by time-resolved infrared fluorescence (IRF) near 4.5 μm. Early studies of $N_2O(00^01)$ have relied on preparation by excitation with the N_2O laser or by collisional activation by excited CO. Bates *et al.*[1] used the N_2O laser to prepare $N_2O(00^01)$ and they reported the deactivation by ground-state N_2O molecules at 298 K. Yardley[2] also used the N_2O laser to prepare $N_2O(00^01)$ in studies of vibrational relaxation at 298 K by various collision partners including He, Ne, Ar, Kr, H_2, D_2, and N_2O (self-deactivation). Doyennette *et al.* used the N_2O laser to prepare $N_2O(00^01)$ for studies of self-relaxation and gas-surface collisions,[3,4] collisions with $^{14}N_2$ and $^{15}N_2$ over the temperature range 150–1200 K,[5] collisions with HCl

over the temperature range 300–700 K,[6] and collisions with HBr over the temperature range 300–900 K.[7] Mehl *et al.*[8] prepared $N_2O(00^01)$ by the same method and studied the vibrational relaxation of the $N_2O(00^01)$ by a series of deuterated methanes. Hancock and co-workers[9,10] prepared $N_2O(00^01)$ by collisional pumping from CO ($v=1$) excited with a frequency-doubled CO_2 laser and measured the vibrational deactivation by N_2O, CO, and Ar over the temperature range 144–405 K.

While direct pumping of CO_2 with a CO_2 laser is obvious and has long been used, it has been shown only recently that N_2O can be pumped directly by a CO_2 laser.[11] It turns out that the $P(18)$ line of the CO_2 laser at 9.536 μm matches the $(00^01, j=7\leftarrow02^00, j=8)$ transition in N_2O. An advantage of the CO_2 laser over the N_2O laser as a pumping source is that the former is more powerful. Using this method, McNesby and Bates[12] studied the deactivation of $N_2O(00^01)$ by unexcited N_2O over the temperature range 232–365 K. More recently, Siddles *et al.*[13] used the HBr laser for direct excitation of N_2O to $N_2O(00^01)$ and then the temperature-dependent collision rate constants with N_2O, O_2, N_2, and CH_4 were measured. To the best of our knowledge, the above are the only published laser-based (direct and indirect) deactivation studies of $N_2O(00^01)$. The results for near room temperature (295–300 K) are summarized in Table I. Note that the two published results for deactivation by N_2 are markedly different. The reason is that as with the analogous CO_2–N_2 system,[14] two relaxation rates are expected (i.e., a double exponential decay of the IRF), one corresponding to a fast single quantum $V-V$ transfer

TABLE I. Summary of previous laser-based studies of the collisional deactivation of N$_2$O(00^{0}1) near room temperature.

| Collider, M	Excitation method	Deactivation rate constant, $10^{-3}\,k_{N_2O-M}$ (Torr^{-1} s^{-1})[a]	Reference
N$_2$O	N$_2$O laser	0.673±0.009	1
	N$_2$O laser	0.756±0.015	2
	N$_2$O laser	0.730	3
	N$_2$O laser	0.720	6
	N$_2$O laser	0.740	8
	CO$_2$ laser	0.723±0.002	11,12
	HBr laser	0.753±0.003	13
	N$_2$O laser	0.745±0.037	4
	collisional pumping	0.755±0.015	9
	collisional pumping	0.714	10
He	N$_2$O laser	0.261±0.016	2
Ne	N$_2$O laser	0.097±0.009	2
Ar	N$_2$O laser	0.103±0.008	2
	collisional pumping	0.120±0.025	9
	collisional pumping	0.073	10
Kr	N$_2$O laser	0.054±0.006	2
H$_2$	N$_2$O laser	5.58±0.45	2
D$_2$	N$_2$O laser	1.09±0.09	2
N$_2$	N$_2$O laser	4.9[b]	5
	HBr laser	0.269±0.007	13
^{15}N$_2$	N$_2$O laser	8.3[b]	5
O$_2$	HBr laser	0.311±0.02	13
CO	collisional pumping	0.537,225.0[c]	10
HCl	N$_2$O laser	1.5	6
HBr	N$_2$O laser	36	7
CH$_4$	N$_2$O laser	5.4±1.4	8
	HBr laser	4.91±0.33	13
CH$_3$D	N$_2$O laser	40±4	8
CH$_2$D$_2$	N$_2$O laser	86±5	8
CHD$_3$	N$_2$O laser	145±5	8
CD$_4$	N$_2$O laser	199±12	8

[a]The values shown for Ref. 2 have been converted from the reported values for $P\tau$ given in μs atm units where τ is the vibrational relaxation time, and the values shown for Ref. 13 have been converted from the reported deactivation rate constants given in units of cm^3 molecule^{-1} s^{-1}.
[b]N$_2$O(00^{0}1)–N$_2$ V–V exchange.
[c]N$_2$O(00^{0}1)–CO V–V exchange.

$$N_2O(00^01)+N_2(v=0)\rightarrow N_2O(00^00)+N_2(v=1)$$
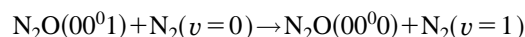
and the other corresponding to a slower V–T transfer

$$N_2O(00^01)+N_2(v=0)\rightarrow N_2O(11^00)+N_2(v=0).$$
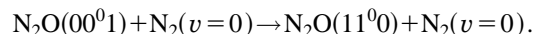
The results of Doyennette et al.[5] are for the former and those of Siddles et al.[13] are for the latter.

We have carried out a series of experiments on the collisional deactivation of CO$_2$(00^{0}1) and N$_2$O(00^{0}1) at ambient temperature (295±2 K). Most of the colliders were large polyatomic molecules. In these experiments the excited CO$_2$ and N$_2$O were prepared by direct pumping with a CO$_2$ laser and monitored by time-resolved IRF [the (00^{0}1)→(00^{0}0) spontaneous emission near 4.3 μm for CO$_2$ and 4.5 μm for N$_2$O]. Results on the deactivation of vibrationally excited CO$_2$ have been reported previously[15] and here we report on results for the deactivation of vibrationally excited N$_2$O. Collisional deactivation rates have been measured for Ar, H$_2$, N$_2$O and the large polyatomic colliders, cyclohexene (c-C$_6$H$_{10}$), cyclohexane (c-C$_6$H$_{12}$), benzene (C$_6$H$_6$), benzene-d$_6$ (C$_6$D$_6$), toluene (C$_7$H$_8$), toluene-d$_8$ (C$_7$D$_8$),

fluorobenzene (C$_6$H$_5$F), p-difluorobenzene (p-C$_6$H$_4$F$_2$), pentafluorobenzene (C$_6$HF$_5$), and hexafluorobenzene (C$_6$F$_6$).

II. EXPERIMENT

The apparatus and experimental procedures have been described in detail previously.[15] Briefly, infrared radiation from a pulsed CO$_2$ laser was directed into a cylindrical cell (400 mm length, 25 mm diam) fitted with NaCl end windows. The production of N$_2$O(00^{0}1) was achieved by tuning the CO$_2$ laser to the P(18) line at 9.536 μm which is coincident with the (00^{0}1, j=7←02^{0}0, j=8) transition in N$_2$O to within 0.002 cm^{-1}.[11] The IRF from excited N$_2$O near 4.5 μm was observed through a sapphire side window and an appropriate bandpass filter by a InSb infrared photovoltaic detector equipped with a matched preamplifier. The output of the detector/preamplifier was further amplified, captured by a digital storage oscilloscope and transferred to a laboratory computer for analysis.

In measurements of the deactivation of N$_2$O(00^{0}1) by the large collider gases, the N$_2$O pressure was 102±3 mTorr and collider gas pressures were in the range 10–100 mTorr while for the deactivation of N$_2$O(00^{0}1) by unexcited N$_2$O the pressure range was 1–30 Torr. The N$_2$O pressures were chosen (by experiment) to minimize self-absorption and heterogeneous deactivation in the fluorescence cell of specified geometry and dimensions used in our experiments. The higher N$_2$O pressure range could not be used in the experiments with added collider gas because the required collider gas pressures then yielded decay rates too fast to measure. All measurements were made at ambient temperature (295±2 K).

N$_2$O (Aldrich, 99%), Ar (BOC Gases, ultrahigh purity), and H$_2$ (J. T. Baker, ultrapure) were used directly as supplied. c-C$_6$H$_{10}$ (Koch-Light, ⩾99.9%), c-C$_6$H$_{12}$ (Merck, 99.7%), C$_6$H$_6$ (BDH, ⩾99.7%), C$_6$D$_6$ (Aldrich, 99.5 atoms% D), C$_7$H$_8$ (Ajax Unilab, 98%), C$_7$D$_8$ (Aldrich, 99+ atoms% D), C$_6$H$_5$F (Merck, 99%), p-C$_6$H$_4$F$_2$ (Aldrich, 99+%), C$_6$HF$_5$ (Aldrich, 99%) and C$_6$F$_6$ (Aldrich, 99.9%) were degassed using several freeze–pump–thaw cycles prior to use.

III. RESULTS

Figure 1 shows a typical set of IRF decay curves for N$_2$O with various pressures of p-C$_6$H$_4$F$_2$ collider gas. The fluorescence decays are fitted well by a single exponential for all collider gases. The observed relaxation times are very much faster than the radiative lifetime of 4.1 ms for N$_2$O(00^{0}1)[2] therefore the loss of excitation via spontaneous IR emission is negligible under the experimental conditions. The Marquardt algorithm[16] for nonlinear least-squares fitting was used to fit each decay curve with a single exponential function of the form

$$I=I_0\exp(-k_{obs}t)+B, \tag{1}$$

where I is the fluorescence intensity, k_{obs} is the pseudo-first-order decay rate constant (inverse of the relaxation time), and B is the nominal baseline. The first-order decay rate constants exhibit a linear increase with collider gas pressure.
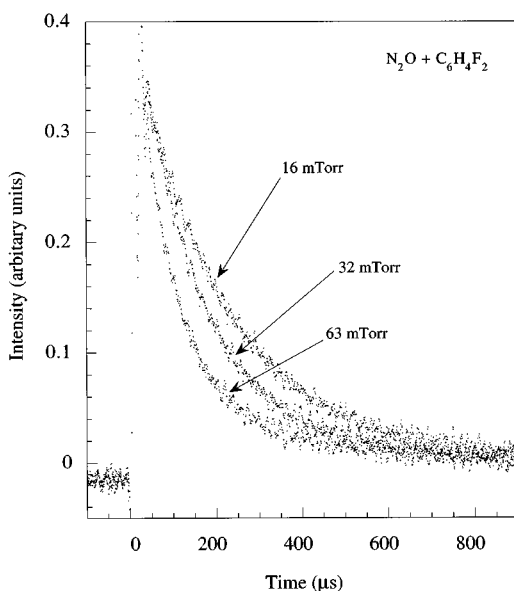
FIG. 1. Infrared fluorescence decay curves for $N_2O(00^01)$ in the presence of the indicated pressures of p-$C_6H_4F_2$ collider gas. $P_{N_2O} = 102$ mTorr.

FIG. 3. Plot of k_{obs} for the deactivation of $N_2O(00^01)$ vs pressure of C_7H_8 and C_7D_8 collider gases. The point shown by the symbol $\diamond$ is the value for 102 mTorr of pure N_2O under the experimental conditions. The error bars correspond to two standard deviations. The lines are the weighted linear-least-squares fittings.

Figures 2 and 3 show typical plots of k_{obs} vs collider gas pressure for C_6H_6, C_6D_6, C_7H_8, C_7D_8, and C_6F_6. Also shown are the weighted linear least-squares fittings. The slope of the k_{obs} vs pressure plot yields the bimolecular deactivation rate constant, k_{N_2O-M} where M represents the collider gas. Note that the intercepts are within experimental error of the measured first-order decay rate for 102 mTorr of pure N_2O (2045 ± 394 s^{-1}) in the fluorescence cell under the experimental conditions. This is in accord with expectation and is analogous to our experiments on the deactivation of
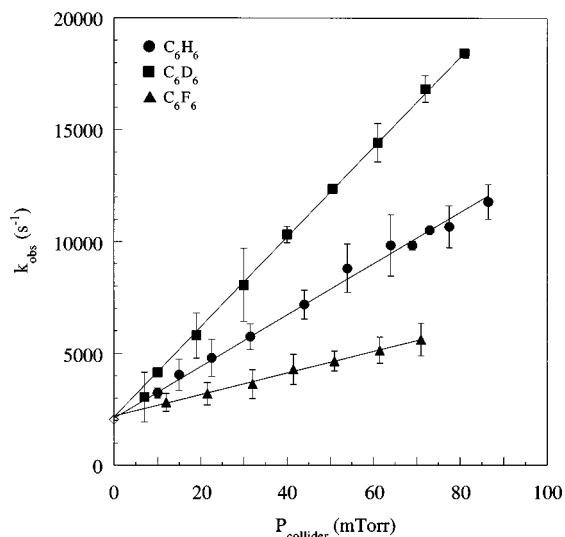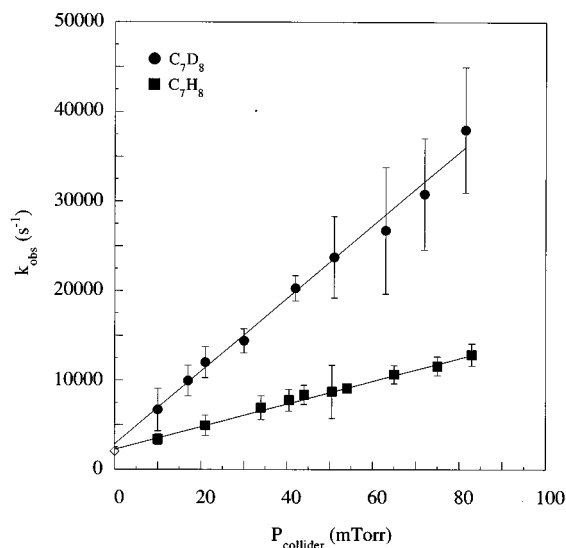
$CO_2(00^01)$.[15] The decay rate for 102 mTorr of N_2O in our experiments contains a contribution from heterogeneous deactivation. Diffusion with heterogeneous deactivation leads to upward curvature in decay rate vs pressure plots at low pressure and the decay rate is also a function of cell geometry (the diameter is the key parameter for long cylindrical cells).[4,17,18] Our measured decay rate of 2045 s^{-1} for 102 mTorr of N_2O in a cylindrical cell of 25 mm diam is consistent with the measurements of 2952, ~1505, and 1410 s^{-1}, respectively obtained by Doyennette et al.[3,4] for 100 mTorr of N_2O in cylindrical cells of diameter 16.5, 27.7, and 30 mm, respectively. (We have also carried out extensive studies of heterogeneous deactivation of CO_2, N_2O, and other species;[16] details will be reported in future manuscripts.) When the collider gases are added to the 102 mTorr of N_2O, heterogeneous deactivation is no longer important, as is evident from the linearity of the plots shown in Figs. 2 and 3. The bimolecular deactivation rate constants for all colliders are summarized in Table II. The errors quoted correspond to 2σ statistical errors from the weighted linear least-squares analysis plus estimated uncertainties in pressure.

The bimolecular deactivation rate constant of $(0.763\pm0.006)\times10^3$ Torr^{-1} s^{-1} obtained for N_2O self-relaxation is in very good agreement with all previous studies except the value reported by Bates et al.[1] which is low comparison (see Table I). The averaged literature value, excluding the measurement of Bates et al., is 0.737×10^3 Torr^{-1} s^{-1}. The rate constants obtained for deactivation by Ar and H_2 agree within experimental uncertainties with the results of Yardley[2] and Hancock et al.[9,10] for Ar, and the results of Yardley[2] for H_2.

In comparing the intrinsic ability of the colliders to deactivate $N_2O(00^01)$, the deactivation rate constants must be

FIG. 2. Plot of k_{obs} for the deactivation of $N_2O(00^01)$ vs pressure of C_6H_6, C_6D_6, and C_6F_6 collider gases. The point shown by the symbol $\diamond$ is the value for 102 mTorr of pure N_2O under the experimental conditions. The error bars correspond to two standard deviations. The lines are the weighted linear-least-squares fittings.

TABLE II. Bimolecular rate constants, deactivation probabilities and average energy transfer for the vibrational deactivation of $N_2O(00^01)$ at ambient temperature (295 ± 2 K).

Collider, M	Deactivation rate constant, $10^{-3} k_{N_2O-M}$ (Torr^{-1} s^{-1})	Deactivation probability ($\times 10^3$)		$-\langle \Delta E \rangle^a$ (cm^{-1})
		Hard-sphere, P_{HS}	Lennard-Jones, P_{LJ}	
N_2O	0.763 ± 0.006			
Ar	0.103 ± 0.003	0.0138	0.0109	
H_2	4.89 ± 0.52	0.293	0.248	
c-C_6H_{10}	176 ± 10	16.7	10.2	23
c-C_6H_{12}	153 ± 22	14.2	8.71	19
C_6H_6	115 ± 4	11.7	7.06	16
C_7H_8	127 ± 11	11.6	7.08	16
C_6D_6	201 ± 2	20.7	12.5	28
C_7D_8	407 ± 52	37.6	23.0	51
C_6H_5F	144 ± 14	14.5	8.86	20
p-$C_6H_4F_2$	173 ± 13	17.1	10.4	23
C_6HF_5	129 ± 8	12.9	7.89	18
C_6F_6	48 ± 9	4.78	2.93	7

[a]Based on $1/P_{LJ}$ and deactivation to $N_2O(00^00)$.

scaled to account for the different masses, sizes, and velocities of the colliders. The deactivation rate constants have been scaled to both the Lennard-Jones collision rate constant, k_{LJ} and the hard-sphere collision rate constant, k_{HS}. These scalings yield deactivation probabilities, P_{LJ} and P_{HS}. The values obtained are shown in Table I. The values used for the Lennard-Jones collision rate constant, k_{LJ} were calculated using the method and data sources described previously.[15]

IV. DISCUSSION

The measured deactivation rate constants for the large polyatomic colliders are very large. They are up to several orders of magnitude larger than the values for monatomics, diatomics and the small polyatomic, methane (nondeuterated). The same relativities are exhibited by the deactivation probabilities. The lowest measured deactivation probability in the group of polyatomic colliders is the value of $P_{LJ} = 2.93 \times 10^{-3}$ for C_6F_6 (the only large molecule studied without C–H or C–D stretch modes). The value is only 0.42 times that for the hydrocarbon analogue, C_6H_6 (the reduction is essentially the same for P_{HS} and k_{N_2O-M} as well as P_{LJ}). For the deactivation of $CO_2(00^01)$ by the same two species the reduction is less pronounced with the value for C_6F_6 being 0.77 times that for C_6H_6.

In contrast to C_6F_6, C_6D_6 has a P_{LJ} which is 4.3 times that for C_6F_6. The value of P_{LJ} for C_7D_8 is even greater than that for C_6D_6 (a factor of 1.8 times larger) and very much greater than the values for the remaining colliders. These two values are the highest observed in the group. The enhancement of the deactivation probability by perdeuteration of the collider is also shown by a comparison of the values for C_6H_6 vs C_6D_6, and for C_7H_8 vs C_7D_8. The effect of deuteration is only a factor 1.8 for the benzenes but increases dramatically to a factor of 3.2 for the toluenes. Mehl *et al.*[8] reported hard-sphere deactivation probabilities for both $CO_2(00^01)$ and $N_2O(00^01)$ with a series of deuterated methanes. The values were found to be identical for deactivation

of $CO_2(00^01)$ or $N_2O(00^01)$ by the same collision partner and they were found to increase linearly with the number of deuterium atoms per substituted methane. The Mehl *et al.*[8] values of P_{HS} for $N_2O(00^01)$ are 20×10^{-3}, 14×10^{-3}, 8.2×10^{-3}, and 3.7×10^{-3} for CD_4, CD_3H, CD_2H_2, and CDH_3, respectively. The average of these values on a per C–D stretch basis is 4.4×10^{-3}. Our measured value of P_{HS} for C_7D_8 is 37.6×10^{-3} so the effective value per C–D stretch is 4.7×10^{-3} (without differentiating between the C–D stretch modes on the benzene ring and those on the methyl group). Likewise the effective value per C–D stretch in the case of C_6D_6 is 3.5×10^{-3}. The average of these two values is 4.1×10^{-3}, which is in excellent agreement with the average value from the results of Mehl *et al.*[8]

The deactivation probabilities for the remaining colliders fall in between the value for C_6F_6 and the values for the perdeuterated species. The values of P_{LJ} for c-C_6H_{12}, C_6H_6, C_7H_8, C_6HF_5, and C_6H_5F are essentially the same within experimental error (average 7.92×10^{-3}) while those for c-C_6H_{10} and $C_6H_4F_2$ are the essentially same within experimental error (average 10.3×10^{-3}). The relatively small difference in deactivation probability between these two groups of molecules may not be significant.

Siddles *et al.*[13] have compared the rate constants for deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by self-relaxation, N_2, O_2, and CH_4. The rate constant ratios at 300 K are 2.3, 2.6, 2.3, and 1.1, respectively. Siddles *et al.*[13] state that the higher rate constants for $N_2O(00^01)$ relative to $CO_2(00^01)$ ''is a general feature of the behavior of $N_2O(00^01)$ and has been seen for a wide range of relaxants.'' However a survey of the literature shows that this is true only for self-relaxation and deactivation by monatomics and some diatomics. Studies of both excited species in the same laboratory by Doyennete *et al.*[6,7] yield rate constant ratios of 0.33 and 0.27 for deactivation by HCl and HBr, respectively and the comparative studies of Mehl *et al.*[8] yield rate constant ratios near unity for deactivation by a series of deuterated methanes.
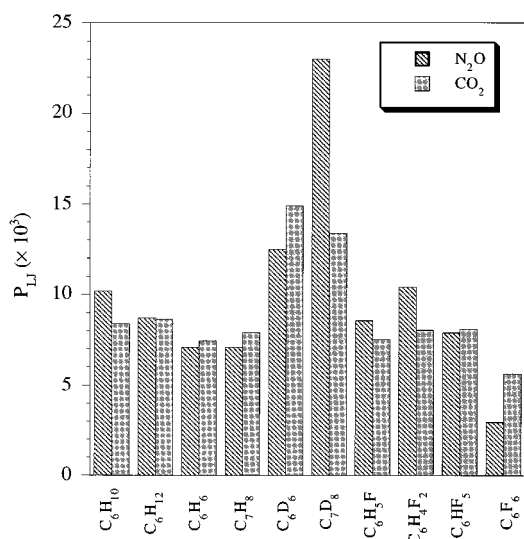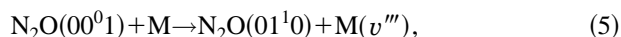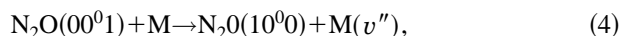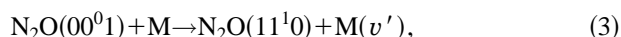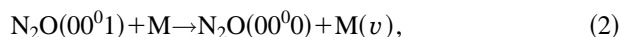
FIG. 4. Magnitudes of P_{LJ} for the deactivation of $N_2O(00^01)$ and $CO_2(00^01)$ by large polyatomic colliders.

The rate constants obtained by us for the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by the same set of large polyatomic colliders also are similar in magnitude except for the colliders C_6F_6 and C_7D_8. This is reflected in the deactivation probabilities which are compared in Fig. 4. The rate constant or deactivation probability ratios are 0.5 for C_6F_6 and 1.7 for C_7D_8. A rationale for the different behavior by these two collision partners is given below.
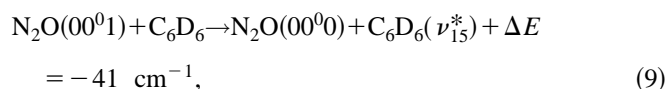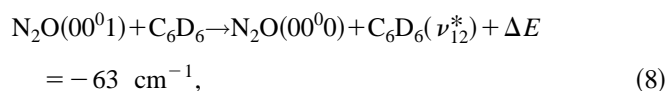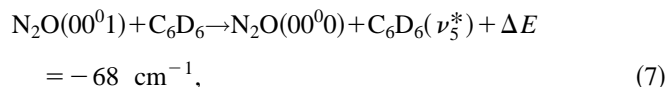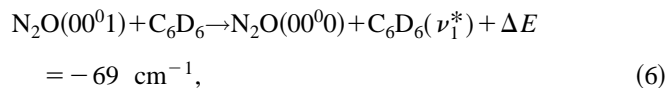
The homogeneous deactivation processes through which $N_2O(00^01)$ may lose its energy are inter- and intramolecular $V-V$ energy transfer and $V-T/R$ energy transfer. In the present work, the measured deactivation rate constant contains all these possible pathways for energy loss from the excited molecule following collisions with the collider gas. However because the measured rates are large, and because the processes involving $V-T/R$ transfer are normally slow,[19] the measured deactivation rate constant and deactivation probability for the large polyatomic colliders mostly reflects $V-V$ energy transfer. The following $V-V$ deactivation processes are possible:
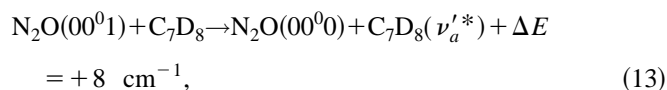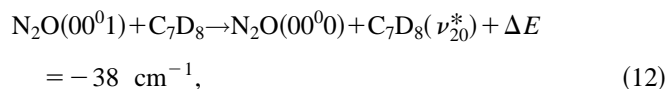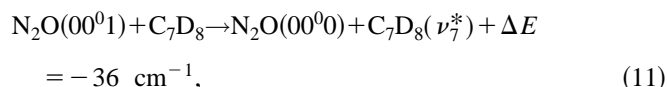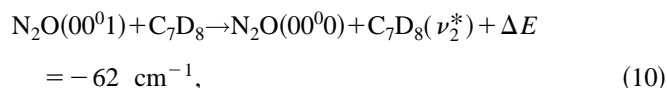
$$N_2O(00^01)+M\rightarrow N_2O(00^00)+M(v), \tag{2}$$

$$N_2O(00^01)+M\rightarrow N_2O(11^10)+M(v'), \tag{3}$$

$$N_2O(00^01)+M\rightarrow N_2O(10^00)+M(v''), \tag{4}$$

$$N_2O(00^01)+M\rightarrow N_2O(01^10)+M(v'''), \tag{5}$$

where $M(v)$, $M(v')$, $M(v'')$, $M(v'')$, $M(v''')$ is the polyatomic collision partner with excitation in sufficient vibrations to account for the energy loss from $N_2O(00^01)$. The relative contributions of processes (2)–(5) to the overall deactivation of $N_2O(00^01)$ depends on the nature of the collision partner, M. Equation (2) is intermolecular $V-V$ energy transfer involving deactivation of $N_2O(00^01)$ directly to the vibrational ground state and hence allows 2224 cm⁻¹ to be available to the collision partner. Colliders that have a vibrational fre-
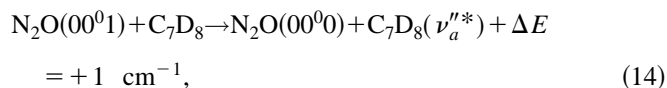
quency close to 2224 cm⁻¹ will be collisionally excited to that frequency. Such a process is very efficient since it involves minimum vibrational quantum number change. Colliders that do not have a vibrational frequency close to 2224 cm⁻¹ are still able to accept the available energy if the summation of two (or more) of its vibrational frequencies is close to 2224 cm⁻¹. The two important factors that control intermolecular $V-V$ energy transfer are the value of the energy gap or mismatch, ΔE (in this study the difference between 2224 cm⁻¹ for $N_2O(00^01)$ and the value of the collisionally excited mode in the collider), and the quantum number change.[19] The most favored $V-V$ channels are those associated with the smallest ΔE and the fewest quantum number changes. Simple theoretical considerations indicate that the efficiency of collisional deactivation is reduced by about a factor of 10 for each quantum number change and reduced by about a factor of 10 for each 200 cm⁻¹ of ΔE.[19]

In the large polyatomic colliders there are many vibrational modes and energy from $N_2O(00^01)$ may be transferred to any one of them. The values[20,21] for the C–D stretching frequencies in C_6D_6 and C_7D_8 places them in near resonance ($\Delta E<100$ cm⁻¹) with the (00^01) vibrational level in N_2O. Thus for C_6D_6 collider the following four single quantum near-resonant channels (within the range 2224 ± 100 cm⁻¹)[20] resulting in direct deactivation of $N_2O(00^01)$ to the vibrational ground state are available:

$$N_2O(00^01)+C_6D_6\rightarrow N_2O(00^00)+C_6D_6(\nu_1^*)+\Delta E$$
$$=-69 \text{ cm}^{-1}, \tag{6}$$

$$N_2O(00^01)+C_6D_6\rightarrow N_2O(00^00)+C_6D_6(\nu_5^*)+\Delta E$$
$$=-68 \text{ cm}^{-1}, \tag{7}$$

$$N_2O(00^01)+C_6D_6\rightarrow N_2O(00^00)+C_6D_6(\nu_{12}^*)+\Delta E$$
$$=-63 \text{ cm}^{-1}, \tag{8}$$

$$N_2O(00^01)+C_6D_6\rightarrow N_2O(00^00)+C_6D_6(\nu_{15}^*)+\Delta E$$
$$=-41 \text{ cm}^{-1}, \tag{9}$$

where the asterisk represents the vibrationally excited mode in the collider and ν_1, ν_5, ν_{12}, and ν_{15} are the C–D stretch modes. For C_7D_8 collider the near-resonant channels[21] are

$$N_2O(00^01)+C_7D_8\rightarrow N_2O(00^00)+C_7D_8(\nu_2^*)+\Delta E$$
$$=-62 \text{ cm}^{-1}, \tag{10}$$

$$N_2O(00^01)+C_7D_8\rightarrow N_2O(00^00)+C_7D_8(\nu_7^*)+\Delta E$$
$$=-36 \text{ cm}^{-1}, \tag{11}$$

$$N_2O(00^01)+C_7D_8\rightarrow N_2O(00^00)+C_7D_8(\nu_{20}^*)+\Delta E$$
$$=-38 \text{ cm}^{-1}, \tag{12}$$

$$N_2O(00^01)+C_7D_8\rightarrow N_2O(00^00)+C_7D_8(\nu_a'^*)+\Delta E$$
$$=+8 \text{ cm}^{-1}, \tag{13}$$

$$N_2O(00^01)+C_7D_8 \rightarrow N_2O(00^00)+C_7D_8(\nu_a''^*)+\Delta E$$

$$= +1 \text{ cm}^{-1}, \tag{14}$$

where the asterisk represents the vibrationally excited mode in the collider and ν_2, ν_7, and ν_{20} are C–D stretch modes on the benzene ring and ν_a' and ν_a'' are the methyl group C–D stretch modes. The major factor contributing to the enhanced deactivation by C$_7$D$_8$ is most likely due to the near perfect match between the ν_3 stretch mode in N$_2$O at 2224 cm^{-1} and the C–D antisymmetric stretch of the methyl group in C$_7$D$_8$ at 2223 cm^{-1} [Eq. (14)]. Even the remaining seven C–D stretches in C$_7$D$_8$ are in near resonance with N$_2$O(00^{0}1), all being within 100 cm^{-1} of 2224 cm^{-1}. Bearing in mind the expected drop in deactivation efficiency with increase in ΔE, the difference between the deactivation of N$_2$O(00^{0}1) and CO$_2$(00^{0}1) by C$_7$D$_8$ is likely to be due to the fact that the ν_3 stretch mode in CO$_2$ occurs at 2349 cm^{-1} and hence the ΔE values for the methyl group C–D stretches in C$_7$D$_8$ become $>$100 cm^{-1}. (The ΔE values for the C–D stretches in the methyl group become 138, 138, and 223 cm^{-1}, respectively while those for the C–D stretches on the benzene ring remain $<$100 cm^{-1}.) We are exploring this matter further by conducting experiments with C$_6$H$_5$CD$_3$ and C$_6$D$_5$CH$_3$ as collider gases.[22]

In contrast to C$_6$D$_6$ and C$_7$D$_8$ the nondeuterated colliders do not have any vibrational modes in near resonance with N$_2$O(00^{0}1). The relatively low deactivation probability for C$_6$F$_6$ is most likely due to the energy transfer occurring via energy sharing processes involving multiple quantum number changes. C$_6$F$_6$ has many low vibrational frequencies,[23] and therefore high density of states. In fact there are more than 5729 (overtone and combination) vibrational states in the range of 2224$\pm$1 cm^{-1} which are in close resonance with the (00^{0}1) vibrationally excited state in N$_2$O, and more than 8000 vibrational states in the range of 2349$\pm$1 cm^{-1} which are in close resonance with the (00^{0}1) vibrationally excited state in CO$_2$. These are possible open channels for the complete deactivation of N$_2$O(00^{0}1) or CO$_2$(00^{0}1) through intermolecular V–V energy transfer. However, for the energy to be transferred through such channels, many vibrational modes in the collider have to be excited simultaneously during the collision (multiple quantum change). Therefore despite its properties, C$_6$F$_6$ shows the lowest deactivation probability of the group. More definitive arguments about which processes are contributing to the deactivation of N$_2$O(00^{0}1) by the different collider gases would require information about the final states of the N$_2$O following deactivation.

An estimate of the average energy removed per collision, $-\langle\Delta E\rangle$ may be obtained from the ratio of the energy loss from the molecule to the number of collisions required for this deactivation. Assuming that the data represent direct transfer between N$_2$O(00^{0}1) and the vibrational ground state, then $-\langle\Delta E\rangle$ values may be obtained by dividing 2224 cm^{-1} by the number of collisions or $1/P_{\text{LJ}}$. The values of $-\langle\Delta E\rangle$ so calculated are listed in Table II. These values represent the maximum possible $-\langle\Delta E\rangle$. The $-\langle\Delta E\rangle$ values found for the C$_6$D$_6$ and C$_7$D$_8$ colliders are 1.8 and 3.2 times the respective values for the C$_6$H$_6$ and C$_7$H$_8$ colliders.

ACKNOWLEDGMENTS

[1] R. D. Bates, G. W. Flynn, and A. M. Ronn, J. Chem. Phys. **49**, 1432 (1968).

[2] J. T. Yardley, J. Chem. Phys. **49**, 2816 (1968).

[3] L. Doyennette, M. Margottin-Maclou, H. Gueguen, A. Carion, and L. Henry, J. Chem. Phys. **60**, 697 (1974).

[4] M. Margottin-Maclou, L. Doyennette, and L. Henry, Appl. Opt. **10**, 1768 (1971).

[5] H. Gueguen, F. Yzambart, A. Chakroun, M. Margottin-Maclou, L. Doyennette, and L. Henry, Chem. Phys. Lett. **35**, 198 (1975).

[6] L. Doyennette, F. Al Adel, A. Chakroun, M. Margottin-Maclou, and L. Henry, J. Chem. Phys. **69**, 5334 (1978).

[7] B. Seoudi, L. Doyennette, M. Margottin-Maclou, A. Chakroun, and L. Henry, Chem. Phys. Lett. **63**, 251 (1979).

[8] R. Mehl, S. A. McNeil, L. Napolitano, L. M. Portal, W. S. Drozdoski, and R. Bates, J. Chem. Phys. **69**, 5349 (1978).

[9] J. K. Hancock, D. F. Starr, and W. H. Green, J. Chem. Phys. **61**, 3017 (1974).

[10] D. F. Starr and J. K. Hancock, J. Chem. Phys. **62**, 3747 (1974).

[11] K. L. McNesby and R. D. Bates, J. Mol. Spectrosc. **136**, 213 (1989).

[12] K. L. McNesby and R. D. Bates, Chem. Phys. **151**, 401 (1991).

[13] R. M. Siddles, G. J. Wilson, and C. J. S. M. Simpson, Chem. Phys. Lett. **225**, 146 (1994).

[14] S. H. Bauer, J. F. Caballero, R. Curtis, and J. R. Wiesenfeld, J. Phys. Chem. **91**, 1778 (1987).

[15] K. L. Poel, Z. T. Alwahabi, and K. D. King, Chem. Phys. **201**, 263 (1995).

[16] D. W. Marquardt, J. Soc. Indust. Appl. Math. **11**, 431 (1963).

[17] L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, Phys. Rev. Lett. **17**, 233 (1966); M. Kovacs, D. R. Rao, and A. Javan, J. Chem. Phys. **48**, 3339 (1968); P. L. Houston and R. P. Merrill, Chem. Rev. **88**, 657 (1988).

[18] K. L. Poel and K. D. King, unpublished work and work in progress.

[19] J. T. Yardley, *Introduction to Molecular Energy Transfer* (Academic, New York, 1980).

[20] T. Shimanouchi, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 39 (1972), p. 153.

[21] N. Fuson, C. Carrigou-Lagrange, and M. L. Josien, Spectrochim. Acta **16**, 106 (1960).

[22] C. M. Stamatoiu and K. D. King, work in progress.

[23] V. J. Eaton and D. Steele, J. Mol. Spectrosc. **48**, 446 (1973); R. A. R. Pearce, D. Steele, and K. Radcliffe, J. Mol. Struct. **15**, 409 (1973); F. Torok, A. Hegeolus, K. Koas, and P. Pauly, *ibid*. **32**, 93 (1976).