Collisional Deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by Toluene Isotopomers: Near-Resonant Energy Transfer from $N_2O(00^01)$

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The time-resolved infrared fluorescence (IRF) technique has been used to study the vibrational deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by $C_6D_5CH_3$ and $C_6H_5CD_3$ at ambient temperature (295 ± 2 K). The bimolecular deactivation rate constants were found to be $(242 \pm 17) \times 10^3$ and $(145 \pm 5) \times 10^3$ $Torr^{-1}$ s^{-1}, respectively, for the deactivation of $CO_2(00^01)$, and $(253 \pm 13) \times 10^3$ and $(376 \pm 20) \times 10^3$ $Torr^{-1}$ s^{-1}, respectively, for the deactivation of $N_2O(00^01)$. Experimental deactivation probabilities are calculated and compared with our previous data for deactivation of the same two excited molecules by the colliders C_6H_6, C_6D_6, $C_6H_5CH_3$, and $C_6D_5CD_3$. All deuterated species show enhanced deactivation relative to the respective nondeuterated species, with the largest effects being exhibited by the deactivation of $N_2O(00^01)$ by $C_6D_5CD_3$ and $C_6H_5CD_3$. The results indicate that the C−D stretch mode in the methyl group of the toluene isotopomers is the major factor responsible for the considerably enhanced deactivation of $N_2O(00^01)$, probably as a result of near-resonant intermolecular V−V energy transfer.

Introduction

Carbon dioxide and nitrous oxide have been used as 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. CO_2 has long been used in this role (see, for example, refs 1−12), but the studies of N_2O began much more recently and are far less extensive.[13−25] Most experimental measurements have been confined to deactivation of both CO_2 and N_2O excited to the (00^01) vibrational level of the asymmetric stretch mode, ν_3.

In previous work,[26,27] we carried out a series of experiments on the collisional deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by mostly large polyatomic molecules at ambient temperature (295 ± 2 K). The excited CO_2 and N_2O were prepared by direct pumping with a CO_2 laser and monitored by time-resolved infrared fluorescence (IRF) (the $(00^01) \rightarrow (00^00)$ spontaneous emission near 4.3 μm for CO_2 and 4.5 μm for N_2O). The bimolecular 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 determined and then scaled to the hard-sphere and Lennard-Jones collision rate constants to yield deactivation probabilities, P_{HS} and P_{LJ}. For both $CO_2(00^01)$ and $N_2O(00^01)$ there was little difference in the deactivation probabilities between the acyclic ring compounds and their aromatic analogues and the partially fluorinated benzenes, but C_6F_6 was found to be much less efficient than the other species. The perdeuterated species, C_6D_6 and $C_6D_5CD_3$, especially the latter, showed considerably enhanced deactivation relative to the other species. The effect was a factor of about 2 for C_6D_6 and a factor of more than 3 for $C_6D_5CD_3$. In order to differentiate between the effects of the C−D stretch mode in the aromatic ring and the C−D stretch mode in the methyl group, we have now carried out experiments with $C_6H_5CD_3$ and $C_6D_5CH_3$ as collider gases.

Experimental Section

The apparatus and experimental procedures have been described in full detail previously.[26,27] Briefly, infrared radiation from a pulsed CO_2 laser was directed into a cylindrical cell fitted with NaCl end windows. The cell was used under static gas conditions with the CO_2 or N_2O pressure at 102 ± 3 mTorr and collider gas pressures in the range 10−100 mTorr. The P(21) laser line at 10.6 μm was used to produce excited CO_2 in the $(00^01, j = 21)$ rovibrational state through the $(00^01, j = 21) \leftarrow (10^00, j = 22)$ transition, and the production of the $N_2O(00^01)$ was achieved by tuning to the P(18) laser line at 9.536 μm, which is coincident with the $(00^01,\ j = 7 \leftarrow 02^00,\ j = 8)$ transition in N_2O to within 0.002 cm^{-1}.[23] All collider gases studied are transparent at these laser lines. The pulse-to-pulse energy variations of the laser were ca. ±5%. A fluence of 0.4 J cm^{-2} was used in these experiments.

The IRF from excited CO_2 near 4.3 μm and from excited N_2O near 4.5 μm was observed through a sapphire side window and an appropriate band-pass 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. The detector/preamplifier was shielded by a copper cage to prevent electrical interference from the CO_2 laser. The detector/amplifier rise time is ∼15 μs; IRF decays occur over typically several hundred microseconds. The oscilloscope was used to average decay curves for ∼200 pulses at a laser pulse repetition frequency of ∼1 Hz, in order to achieve good signal-to-noise ratios. All measurements were made at ambient temperature (295 ± 2 K).

CO_2 (Matheson, bone dry) and N_2O (Aldrich, 99%) were used directly as supplied. $C_6D_5CH_3$ (Isotec, Inc., 99+ atom % D) and $C_6H_5CD_3$ (Isotec, Inc., 99+ atom % D) were degassed using several freeze−pump−thaw cycles prior to use.

Results

The IRF decay curves are similar to those obtained previously for $CO_2(00^01)$ and $N_2O(00^01)$ with other collider gases.[26,27] Typical IRF decay curves are shown in Figure 2 of ref 26 for $CO_2(00^01)$ and in Figure 1 of ref 27 for $N_2O(00^01)$. The fluorescence decays are fitted well by a single exponential for all collider gases. For each excited species, the observed relaxation times are very much faster than the respective

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TABLE 1: Bimolecular Rate Constants and Deactivation Probabilities for the Vibrational Deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by Isotopomers of Benzene and Toluene at Ambient Temperature (295 ± 2 K)

excited molecule	collider, M	deactivation rate constant, $10^{-3}k_{A-M}$ (Torr^{-1} s^{-1})	$10^{10}k_{LJ}$ (cm^3 molecule^{-1} s^{-1})	Lennard-Jones deactivation probability, 10^3P_{LJ}	ref
$CO_2(00^{01})$	C_6H_6	120 ± 4	4.93	7.44	26
	C_6D_6	238 ± 9	4.86	14.9	26
	$C_6H_5CH_3$	140 ± 5	5.42	7.89	26
	$C_6D_5CD_3$	234 ± 15	5.35	13.4	26
	$C_6D_5CH_3$	242 ± 17	5.39	13.7	this work
	$C_6H_5CD_3$	145 ± 5	5.43	8.16	this work
$N_2O(00^01)$	C_6H_6	115 ± 4	4.98	7.06	27
	C_6D_6	201 ± 2	4.91	12.5	27
	$C_6H_5CH_3$	127 ± 11	5.48	7.08	27
	$C_6D_5CD_3$	407 ± 52	5.41	23.0	27
	$C_6D_5CH_3$	253 ± 13	5.46	14.2	this work
	$C_6H_5CD_3$	376 ± 20	5.50	20.9	this work

TABLE 2: Channels with ΔE in the Range ±∼100 cm^{-1} for the Deactivation of $CO_2(00^01)$ by Isotopomers of Benzene and Toluene

		no. of channels with 1-QNC[a] or 2-QNC in the colllider	
collider	CO_2 final state	1-QNC	2-QNC
$C_6H_5CH_3$	00^00	0	103
	10^00	8	38
	01^10	2	101
	11^10	3	4
$C_6H_5CD_3$	00^00	1	98
	10^00	12	44
	01^10	2	121
	11^10	3	4
$C_6D_5CH_3$	00^00	5	101
	10^00	5	53
	01^10	2	129
	11^10	4	6
$C_6D_5CD_3$	00^00	6	81
	10^00	10	64
	01^10	1	156
	11^10	5	7
C_6H_6	00^00	0	61
	10^00	7	4
	01^10	2	60
	11^10	2	0
C_6D_6	00^00	6	54
	10^00	6	9
	01^10	0	110
	11^10	2	0

[a] QNC = quantum number change.

TABLE 3: Channels with ΔE in the Range ±∼100 cm^{-1} for the Deactivation of $N_2O(00^01)$ by Isotopomers of Benzene and Toluene

		no. of channels with 1-QNC[a] or 2-QNC in the colllider	
collider	N_2O final state	1-QNC	2-QNC
$C_6H_5CH_3$	00^00	0	108
	10^00	8	33
	01^10	2	102
	11^10	3	5
$C_6H_5CD_3$	00^00	3	111
	10^00	12	38
	01^10	2	113
	11^10	3	5
$C_6D_5CH_3$	00^00	5	120
	10^00	8	49
	01^10	2	131
	11^10	3	7
$C_6D_5CD_3$	00^00	8	40
	10^00	12	64
	01^10	2	157
	11^10	3	9
C_6H_6	00^00	0	85
	10^00	9	4
	01^10	2	68
	11^10	1	0
C_6D_6	00^00	6	72
	10^00	6	11
	01^10	2	98
	11^10	2	0

[a] QNC = quantum number change.

radiative lifetimes of 2.5 ms for $CO_2(00^01)$[1] and 4.1 ms for $N_2O(00^01)$;[14] therefore, the loss of excitation via spontaneous IR emission is negligible under the experimental conditions. The Marquardt algorithm[28] for nonlinear least-squares fitting was used to fit each decay curve with a single-exponential function of the form

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

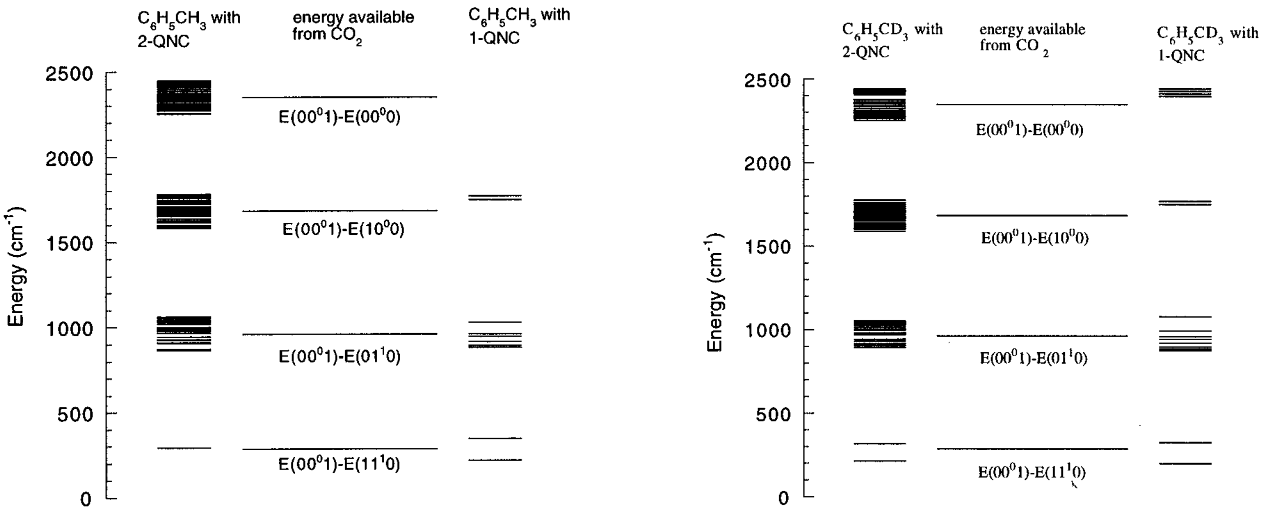
where I is the fluorescence intensity, k_{obs} is the pseudo-first-order decay rate constant (inverse of the relaxation time), and B is the nominal base line. The first-order decay rate constants exhibit a linear increase with collider gas pressure; the plots of k_{obs} versus collider gas pressure obtained in this work are similar to typical plots shown previously (see Figure 3 of ref 26 and Figures 2 and 3 of ref 27).

The slope of the k_{obs} versus pressure plot yields the bimolecular deactivation rate constant, k_{A-M}, where A is CO_2 or N_2O and M represents the collider gas. The k_{A-M} are summarized in Table 1. The errors quoted correspond to 2σ statistical errors from the weighted linear least-squares analysis plus estimated uncertainties in pressure.

In comparing the intrinsic ability of the colliders to deactivate the excited species, the deactivation rate constants must be scaled to account for the different masses, sizes, and velocities of the colliders. The deactivation rate constants have been scaled to the Lennard-Jones collision rate constant, k_{LJ}, to yield the deactivation probabilities, P_{LJ}, shown in Table 1. The values shown for the k_{LJ} were taken, where appropriate, from our previous work[26,27] or were calculated using the method and data sources described previously.[26,27]

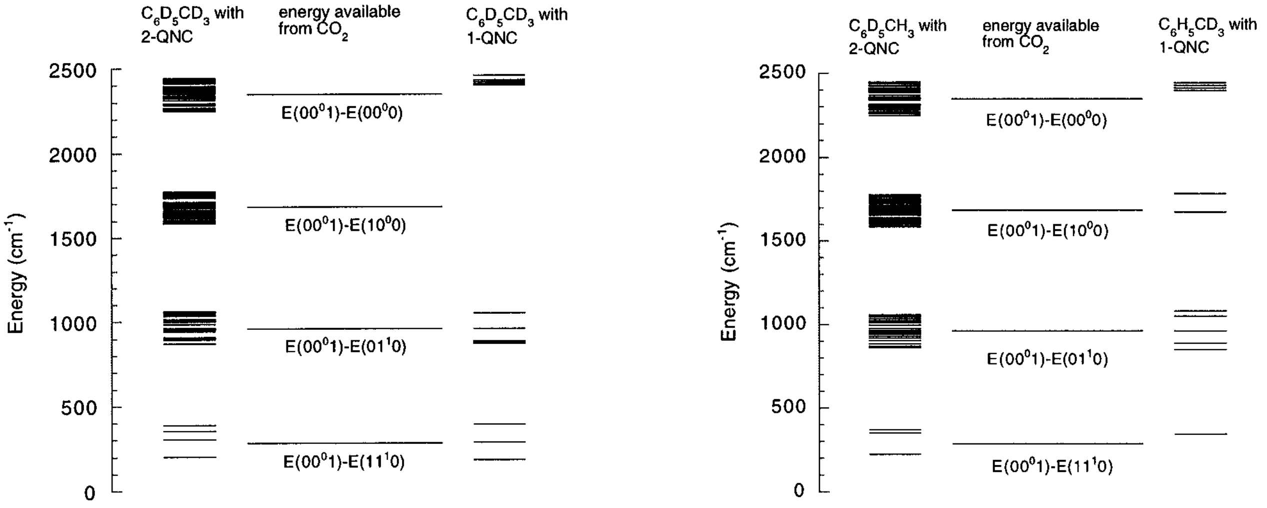
Discussion

The results in Table 1 show that the probabilities for the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by the same set of benzene and toluene isotopomers are similar in magnitude, except for the colliders $C_6H_5CD_3$ and $C_6D_5CD_3$. From our previous results,[26,27] the enhancement of the deactivation probability by perdeuteration of the collider is shown by a comparison of the values for C_6H_6 versus C_6D_6 and for C_7H_8 versus C_7D_8. The effect of perdeuteration is a factor 1.8−2.0 for the deactivation of both $CO_2(00^01)$ and $N_2O(00^01)$ by the benzenes, a factor of 1.7 for deactivation of $CO_2(00^01)$ by the



(a) $CO_2 + C_6H_5CH_3$ system

(b) $CO_2 + C_6H_5CD_3$ system



(c) $CO_2 + C_6D_5CD_3$ system

(d) $CO_2 + C_6D_5CH_3$ system

Figure 1. Energy diagrams for the deactivation of $CO_2(00^01)$ by toluene isotopomers to final vibrational states of CO_2 as shown in processes 2−5. All possible pathways with accompanying changes of one- and two-QNC in the collider are shown, for ΔE in the range $\pm\sim 100$ cm^{-1} (see text). QNC = quantum number change.

toluenes, and a factor of 3.2 for the deactivation of $N_2O(00^01)$ by the toluenes. These results may be compared with those of Mehl et al.,[20] who reported hard-sphere deactivation probabilities for both $CO_2(00^01)$ and $N_2O(00^01)$ with a series of deuterated methanes. Their values were found to be identical for deactivation of $CO_2(00^01)$ or $N_2O(00^01)$ by the same collision partner, and the magnitudes were found to increase linearly with the number of deuterium atoms per substituted methane. That is, the effect of the C−D stretch modes was additive. Our results for the perdeuterated colliders also were shown to be consistent with additivity of the deactivation probability per C−D stretch by treating the contributions of the C−D stretch modes on the benzene ring and those on the methyl group as equivalent. To be more precise, however, the ring and methyl C−D stretch modes should be assigned different deactivation probabilities because of their different vibration frequencies and hence different energy gaps relative to the $CO_2(00^01)$ or $N_2O(00^01)$. These differences are highlighted by the results of the present study.

From the present study, for the deactivation of $CO_2(00^01)$, the P_{LJ} of 13.7 for $C_6D_5CH_3$ is almost the same as the values of 14.9 and 13.4 obtained previously for C_6D_6 and $C_6D_5CD_3$, respectively, while the value of 8.16 for $C_6H_5CD_3$ is almost the same as the values obtained previously for C_6H_6 and $C_6H_5CH_3$. Thus, it is clear that the C−D stretch mode in the aromatic ring and not in the methyl group is responsible for the enhanced deactivation of $CO_2(00^01)$ by the deuterated benzenes and toluenes. On the other hand, for the deactivation of $N_2O(00^01)$, the P_{LJ} of 14.2 for $C_6D_5CH_3$ is a factor of about 2 greater than that obtained previously for $C_6H_5CH_3$ but still much less than the value of 23.0 for $C_6D_5CD_3$. However, the value of 20.9 obtained for $C_6H_5CD_3$ is quite close to the value for $C_6D_5CD_3$. Thus, it is the C−D stretch mode in the methyl group that is responsible for the considerably enhanced deactivation of $N_2O(00^01)$ by the deuterated toluenes. A rationale for the differences in the P_{LJ} for the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by the toluene isotopomers is given below.

As pointed out previously,[26,27] the measured deactivation rate constants for the large polyatomic colliders are very large, being up to several orders of magnitude larger than the values for monatomics, diatomics, and the small polyatomic, methane. The same relativities are exhibited by the deactivation probabilities. These large deactivation rate constants and probabilities are indicative of V−V energy transfer. The many possible V−V deactivation processes for $CO_2(00^01)$ and $N_2O(00^01)$ with large

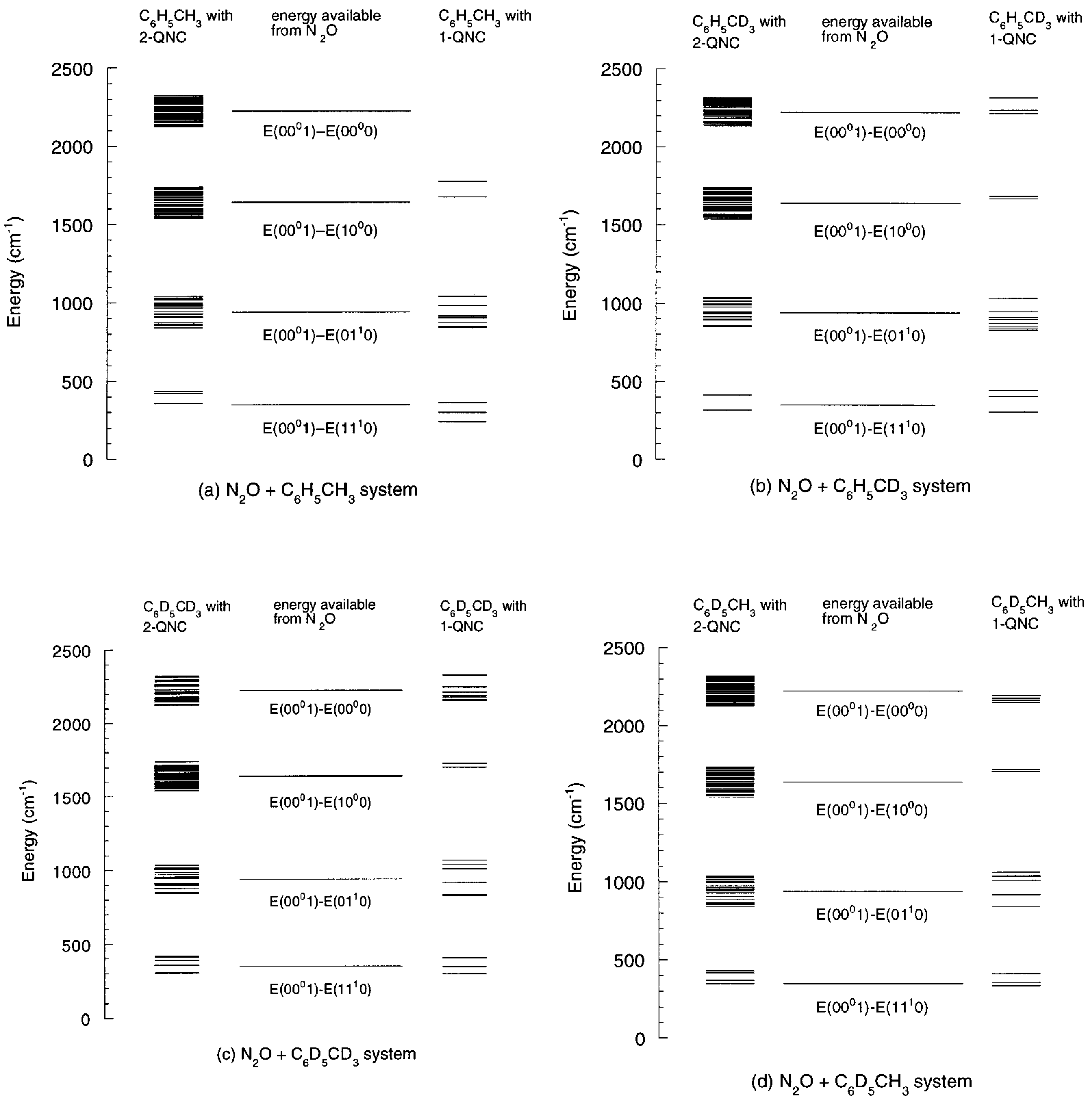


Figure 2. Energy diagrams for the deactivation of $N_2O(00^01)$ by toluene isotopomers to final vibrational states of N_2O as shown in processes 2−5. All possible pathways with accompanying changes of one- and two-QNC in the collider are shown, for ΔE in the range $\pm{\sim}100$ cm^{-1} (see text). QNC = quantum number change.

polyatomic colliders have been discussed previously.[26,27] They are

$$A(00^01) + M \rightarrow A(00^00) + M(v) \tag{2}$$

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

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

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

where A represents CO_2 or N_2O, and $M(v)$, $M(v')$, $M(v'')$, $M(v'')$, or $M(v''')$ is the polyatomic collision partner with excitation in sufficient vibrations to account for the energy change between $A(00^01)$ and the final state of A. The relative contributions of processes 2−5 to the overall deactivation of $A(00^01)$ depends on the nature of the collision partner, M. Determination of exactly which processes are contributing to the deactivation of $A(00^01)$ by the different collider gases would require information about the final states of A following deactivation; however, the final states of the CO_2 and N_2O were not probed in the current study so all possibilities need to be considered. The two important factors that control intermolecular V−V energy transfer are the value of the energy gap or mismatch, ΔE (the difference between $A(00^01)$ and the final state of A, and the value of the collisionally excited mode(s) in the collider), and the quantum number change (QNC).[1] The most favored V−V channels are those associated with a small ΔE (resonant or near-resonant channels) and minimal QNC. Note that simple theoretical considerations indicate that the efficiency of collisional deactivation is reduced by about a factor of 10 for each QNC and reduced by about a factor of 10 for each 200 cm^{-1} of ΔE.[1] For the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by the benzene and toluene isotopomers, we have calculated the number of deactivation channels for all possible deactivation processes 2−5 with a one- or two-QNC in the collider and with ΔE in the range $\pm\sim100$ cm^{-1}. Thus, for these calculations, the overall QNC (counting both the excited species and the collider) ranges from two to six. Possible channels with an overall QNC higher than six would have very low probabilities. The vibrational frequencies for benzene and benzene-d_6 were taken from Shimanouchi[29] and Fuson *et al.*,[30] and those for the toluene isotopomers were taken from Balfour and Fried.[31] The results are summarized in Tables 2 and 3. Figures 1 and 2 show energy diagrams for the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$, respectively, by the toluene isotopomers for processes 2−5 accompanied by a one- or two-QNC in the collider; combination states shown under 2-QNC are all possible pathways that enable the collider to take up the available energy from CO_2 or N_2O and undergo a QNC of two, and states shown under 1-QNC are the pathways for a QNC of one in the collider.

In the deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ the channels with minimum QNC will be those associated with process 2. Here there is a one-QNC in N_2O or CO_2 accompanied by a minimum of a one-QNC in the collider, M resulting in a minimum two-QNC overall. Hence, process 2 with a one-QNC in the collider will dominate the deactivation if there are channels available with a small ΔE. As discussed previously,[26,27] this is the most likely scenario for the deactivation of $N_2O(00^01)$ by $C_6D_5CD_3$ because of the almost exact resonance between the ν_3 stretch mode in N_2O at 2224 cm^{-1} and the C−D antisymmetric stretch of the methyl group in $C_6D_5CD_3$ at 2223 cm^{-1}.[29,30] For the deactivation of $CO_2(00^01)$ by $C_6D_5CD_3$ the ν_3 stretch mode in CO_2 at 2349 cm^{-1} shifts ΔE to outside the range ±100 cm^{-1} for the methyl group C−D stretches in $C_6D_5CD_3$ although for the C−D stretches on the benzene ring the ΔE remain within ±100 cm^{-1}. The channels with an overall three-QNC may occur by either (i) a one-QNC in N_2O or CO_2 accompanied by a two-QNC in the collider or (ii) a two-QNC in N_2O or CO_2 accompanied by a one-QNC in the collider. Thus, channels occurring by (i) will be associated with process 2 with a two-QNC in the collider and channels occurring by (ii) will be associated with process 4 with a one-QNC in the collider. Any channels associated with process 5 will have a minimum four-QNC overall, and any channels associated with process 3 will have a minimum five-QNC overall. It is clear that near-resonant channels with the minimum possible two-QNC overall are available only for the $C_6D_5CD_3$ and $C_6H_5CD_3$ colliders. For the $C_6H_5CH_3$ and $C_6D_5CH_3$ colliders, channels with small ΔE involve a QNC of three or more and hence will have probabilities much less than the two-QNC processes.

Our results have been used for a quantitative test of an interaction model for resonant and near-resonant V−V energy transfer processes between $N_2O(00^01)$ and a large molecule. Shin[32] has been working on the development of such a theoretical model, and he has recently completed calculations for the deactivation of $N_2O(00^01)$ by the colliders C_6H_6, C_6D_6, $C_6H_5CH_3$, and $C_6D_5CD_3$ over the temperature range 100−500 K. In this work, for vibrational transitions involving low-lying energy levels, he used the WKB wave functions to calculate the transition probability in the distorted wave formulation. The applicability of the model was tested against extant data on the intramolecular V−V relaxation of $N_2O(00^01)$ by Ar over the temperature range 144−405 K before being used for large colliders. In agreement with our experimental work, Shin's calculations showed that the deactivation of $N_2O(00^01)$ by C_6D_6 or C_7D_8 is dominated by direct deactivation to the ground state. For example, the calculated deactivation probability for the $N_2O-C_6D_6$ system is 0.0172 compared to our experimental value of 0.0125, and the calculated value for the $N_2O-C_6D_6$ system is 0.0201 compared to our experimental value of 0.0230.

Conclusion

The highly efficient collisional deactivation of $CO_2(00^01)$ and $N_2O(00^01)$ by the polyatomic colliders, $C_6D_5CH_3$ and $C_6H_5CD_3$, has been investigated at ambient temperature (295 ± 2 K) and compared with previous results for deactivation of the same two excited molecules by the colliders C_6H_6, C_6D_6, $C_6H_5CH_3$, and $C_6D_5CD_3$. The results are shown to be consistent with V−V deactivation processes dominated by channels with small ΔE and minimal overall change in quantum number. The exceptionally large probabilities for the deactivation of $N_2O(00^01)$ by $C_6D_5CD_3$ and $C_6H_5CD_3$ are attributed to domination by near-resonant deactivation to $N_2O(00^00)$ because of the almost exact match between the ν_3 stretch mode in N_2O at 2224 cm^{-1} and the C−D antisymmetric stretch of the methyl group at 2223 cm^{-1}. These channels also have the minimum possible overall quantum number change of two. The experimental probabilities for the deactivation of $N_2O(00^01)$ by the polyatomic colliders C_6H_6, C_6D_6, $C_6H_5CH_3$, and $C_6D_5CD_3$ are in close agreement with theoretical calculations based on the WKB wave functions to calculate the transition probability in the distorted wave formulation.[32]

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