

VIBRATIONAL RELAXATION OF $\text{NH}_2[\text{X}^2\text{B}_1(0, v_2, 0)]$ RADICALS

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Received 25 February 1985; in final form 1 July 1985

Energy transfer processes in NH_2 radicals have been studied using the sensitive laser-induced fluorescence (LIF) technique. The NH_2 radicals were generated by infrared multiple-photon dissociation (IR MPD) of monomethylamine (CH_3NH_2), and the state-selected $\text{NH}_2(v_2''=1)$ decay was observed by the LIF detection of $[\text{NH}_2]$. The vibrational relaxation processes studied are $\text{NH}_2(v_2''=1)+\text{M}\rightarrow\text{NH}_2(v_2''=0)+\text{M}$, with $\text{M}=\text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{H}_2, \text{D}_2, \text{N}_2, \text{CO}, \text{O}_2$, and total decay rate of $\text{NH}_2(v_2''=1)$ in the presence of excess CH_3NH_2 . Rate constants of $(3.41\pm 0.03)\times 10^{-13}$, $(1.75\pm 0.09)\times 10^{-13}$, $(3.03\pm 0.08)\times 10^{-13}$, $(3.58\pm 0.06)\times 10^{-13}$, $(13.4\pm 0.5)\times 10^{-13}$, $(4.70\pm 0.19)\times 10^{-13}$, $(4.3\pm 0.3)\times 10^{-13}$, $(5.9\pm 0.4)\times 10^{-13}$, $(9.2\pm 0.5)\times 10^{-13}$, and $8.4\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ were determined for the vibrational deactivation of $\text{NH}_2(v_2''=1)$ by He, Ne, Ar, Kr, H_2 , D_2 , N_2 , CO, O_2 , and CH_3NH_2 , respectively. The effect of the different collision partners on the relaxation rate is discussed. The results can be qualitatively well understood in terms of strong vibration–rotation coupling, due to the small moment of inertia of the NH_2 radicals.

1. Introduction

Energy transfer processes of the type



in which the excess vibrational energy is removed by a collision partner, have been found to be one of the main relaxation channels for vibrationally excited molecules and radicals [1–3]. It is of interest to study the rates of such radical relaxation processes, as well as to observe how they are influenced by different collision partners and experimental conditions. The particular case of vibrationally excited amino radicals $\text{NH}_2(v_2''=1)$ is of special importance in combustion and atmospheric processes [4–6].

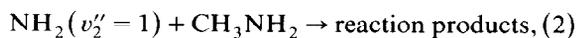
The studies of vibrational energy transfer of H_nX -type molecules and radicals (where X is a heavy atom, such as C, N, F, Cl, Br, etc.) have attracted much interest due to their particular physical properties, i.e. very small moments of inertia, which corresponds to a very fast rotational velocity. The large rotational constants allow large vibrational energy gaps to be narrowed by the various rotational degrees of freedom. The comparison of our experimental results with well-

known vibrational relaxation models has provided valuable insight into the vibrational coupling mechanism.

In a previous publication [7] the influence of the vibrationally excited amino radical on the chemical reactions $\text{NH}_2(0, v_2, 0)+\text{NO}(v''=0)$ was studied. Excitation of the v_2 bending vibration of NH_2 by 17.9 kJ mole^{-1} was found to enhance the reaction rate, while the same amount of rotational and translational excitation (17.9 kJ mole^{-1}) of NH_2 resulted in decreased reactivity in comparison to the room temperature reaction rate [7,8]. In a companion study of the reaction of $\text{NH}_2(0, v_2, 0)+\text{NO}_2$ [9], the excitation of the v_2 vibrational mode retarded the reaction rate. In light of these observations, it is of particular interest to study the dependence of vibrational relaxation of the state-selected NH_2 radicals in collisions with molecules such as O_2 , CO and N_2 , etc., which are similar type relaxation partners and also known to be relevant in combustion and atmospheric processes. Relaxation within the translational or rotational levels of NH_2 radicals occurs in a few gas kinetic collisions, but longer lifetimes can be expected of vibrational states due to the larger energy spacing between the vibrational levels.

It has been demonstrated that infrared multiple-photon dissociation (IR MPD) of selected molecules is an excellent source of radicals, and is a process which produces a non-equilibrium distribution over the different vibrational states [10–13]. The very sensitive laser-induced fluorescence (LIF) method is used to probe the state-selected radicals in order to obtain vibrational relaxation rates induced by M (M = He, Ne, Ar, Kr, H₂, D₂, N₂, CO, O₂) for process (1), with NH₂ in the $v_2 = 1$ level. For simplicity, the NH₂(X²B₁(0, 1, 0)) is referred to in this manuscript as NH₂($v_2'' = 1$).

Due to the fact that a given concentration of precursor molecules is always present in the reaction chamber, it is also necessary to know the extent to which such species contribute to the overall decay of NH₂($v_2'' = 1$) by the following possible processes:

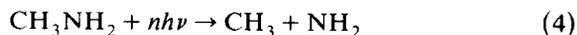


These processes are considered in this study, and their composite reaction rates are also determined.

2. Experimental

The experiments were performed using a Gen-Tec DD-250 CO₂ laser and a Tachisto 550/550G CO₂ laser as the IR MPD pump sources, and a Molelectron UV/400 DL 200 N₂ pumped dye laser as the probe source. The NH₂ radicals were generated by IR MPD of monomethylamine, CH₃NH₂. Monomethylamine is an excellent precursor for NH₂ radicals formed in vibrationally excited states [14,15].

The two possible fragmentation processes for monomethylamine bond breaking for which experimental evidence has been found are the two-center C–N bond breaking [14]



and the two-step process [15]



The NH₂ radicals were generated in a fluores-

cence chamber made of stainless steel. Three sets of entrance and exit windows were set at right angles to each other: one for the CO₂ laser beam for NH₂ radical generation, one for the dye laser beam with which the NH₂ radicals were probed, and the other for collection of the total fluorescence radiation.

The lasers were operated at a 20 pps repetition rate with an output energy < 0.5 J/pulse. Under our experimental conditions, no evidence of NH₂ radicals generated in the vibrationally excited states $v_2'' = 2, 3$ was found and the LIF signals displayed a single exponential decay, so that the effect of cascading from these levels was eliminated. The CO₂ laser beam was tuned to the P(20) line of the 00⁰₁–02⁰₀ transition at 9.552 μm and focused with a 15 cm focal length ZnSe lens through a NaCl window into the cell. The emitted radiation wavelength is within the bandcenter of the ν_8 “C–N stretching” vibration of CH₃NH₂ (overlapping the R branch) [16]. The probe dye laser beam (2 mm diameter) has an energy of 60 μJ and was passed through a series of baffles to reduce the scattered light before it reached the reaction zone.

A 1×10^{-2} M solution of coumarin 485 in ethanol was used in the probe laser to excite the ^PQ_{1,3} transition of the NH₂[A²A₁(0, 13, 0)–X²B₁(0, 1, 0)] band at 533 nm. A low-resolution monochromator, a Jobin–Yvon 0.1 m (2 mm slit width), followed by an EMI 9635B photomultiplier tube (bialkali response) collected the LIF at right angles with respect to the two laser beams. The monochromator was set at 492 nm [A²A₁(0, 13, 0)→X²B₁(0, 0, 0)] to observe the fluorescence from the NH₂($v_2'' = 1$) state. With this experimental arrangement the scattered light was less than one photon per laser shot. The electrical signal was then integrated over the total fluorescence time using a gated integrator (Boxcar PAR 162/164), digitized, and collected by a Nicolet 1070 multichannel averager. The data were then transferred to a Terak 8500 minicomputer for further analysis, and finally plotted using a Tektronix 4662 plotter.

Time decay plots were obtained for varying pressures of M (M = He, Ne, Ar, Kr, H₂, D₂, N₂, CO, O₂) and the corresponding decay rates were determined from semi-log plots of the observed

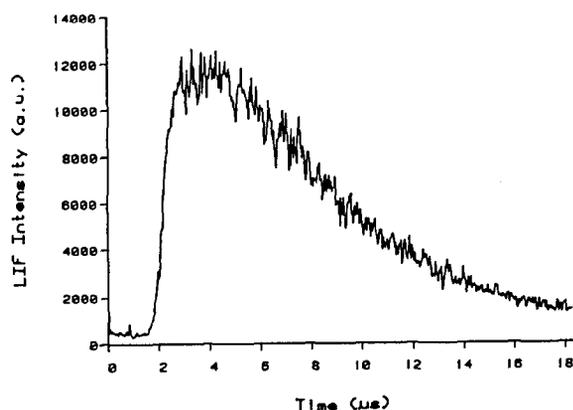


Fig. 1. Laser-induced fluorescence signal intensity from NH₂ ($v_2''=1$) as a function of time for a mixture of 30 mTorr CH₃NH₂ and 8.2 Torr Ne.

time scans. In the very dense time sampling (512 points for each time scan) of the decay curve, the influence of diffusion could be clearly distinguished, because the signal decay in such cases followed a different time behavior than the pseudo-first-order (exponential decay) time behavior shown by relaxation or other possible reactions of NH₂ [11,18]. The pressures were recorded with a Diametrics 570A capacitance manometer.

3. Results and discussion

The time-resolved decay of NH₂ ($v_2''=1$) resulting from IR MPD of 30 mTorr of CH₃NH₂ and 8.2 Torr of Ne is shown in fig. 1. The negative slope of the graph of $\ln(S)$ versus time, where S is

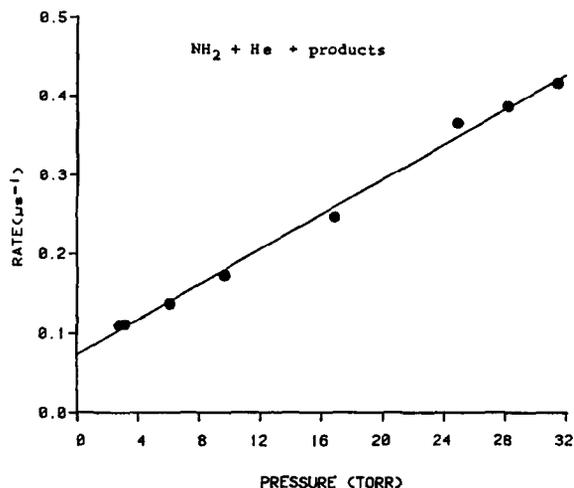


Fig. 2. Pseudo-first-order rate constant values for NH₂ ($v_2''=1$) decay through collisions with He as a function of He pressure. From the slope, the second-order rate constant is obtained.

the NH₂ fluorescence signal intensity, is the pseudo-first-order relaxation rate constant. Fig. 2 shows the variation in the observed decay rate of NH₂ radicals in the first excited vibrational state, NH₂(X ²B₁(0, 1, 0)), versus He pressure. From this type of graph, the second-order decay rate constant for relaxation rate constants for different collision partners are summarized in table 1 along with the probability of relaxation for each collision partner.

3.1. NH₂($v_2''=1$) + inert gas (He, Ne, Ar, Kr)

The vibrational relaxation probabilities of He, Ne, Ar, and Kr, obtained from the decay rates by

Table 1
Vibrational relaxation efficiencies for NH₂ ($v_2''=1$) + M

M	Decay rate $\times 10^{-13}$ (cm ³ molecule ⁻¹ s ⁻¹)	Collision rate ^{a)} $\times 10^{-10}$ (cm ³ molecule ⁻¹ s ⁻¹)	Relaxation probability $\times 10^{-3}$
He	3.41 ± 0.03	3.44	0.99
Ne	1.75 ± 0.99	2.19	0.80
Ar	3.03 ± 0.08	2.40	1.26
Kr	3.58 ± 0.06	2.35	1.52
H ₂	13.4 ± 0.5	5.20	2.58
D ₂	4.70 ± 0.19	3.92	1.20
N ₂	4.3 ± 0.3	2.76	1.56
CO	5.9 ± 0.4	2.68	2.20
O ₂	9.2 ± 0.5	2.48	3.71

^{a)} Calculated using molecular diameters from ref. [19].

the expression $P = k_{\text{obs}}/k_{\text{kin}}$ (where k_{kin} is the kinetic collision rate with hard-sphere cross sections), are plotted versus $\mu^{1/2}$, the square root of the reduced mass of the collision pairs, in fig. 3. The probability of energy transfer decreases from He ($P = 0.99 \times 10^{-3}$) to Ne ($P = 0.88 \times 10^{-3}$), which implies that for light inert collision partners, V-T collision channels may dominate the decay process, which is consistent with the prediction of SSH theory developed by Schwartz, Slawsky and Herzfeld [20] and modified by Tanczos [21] and Stretton [22]. A SSH calculation for the CH₃Cl + He and Ne systems by Knudtson [23] showed a similar trend.

A more striking feature of fig. 3 is exhibited by the monotonic increase of the relaxational probabilities from Ne to Kr. This trend is contrary to that expected on the basis of non-resonant V-T energy transfer theory, e.g., SSH. Since there are no intermolecular V-V or V-R processes involved for the monoatomic collision partners, the excited bending mode of NH₂ ($\nu_2'' = 1497 \text{ cm}^{-1}$) which is the lowest vibrational frequency, cannot relax via intermolecular V-V to the two high-frequency stretches. Thus, it appears that the intramolecular V-R process, induced by inert gas collisions may be the major deactivation channel. For NH₂ radicals, very efficient V-R transfer is quite possible due to the rapid rotational motion associated with hydrogen atoms [24]. Dominant V-R processes

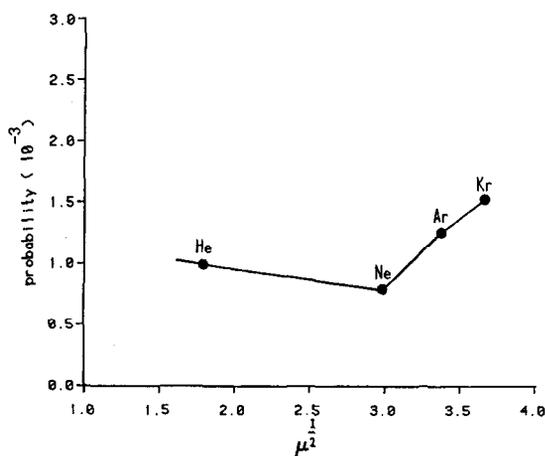
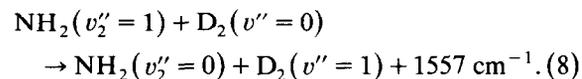
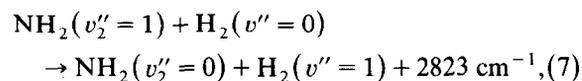


Fig. 3. Energy transfer probability versus square root of the reduced mass of the collision pairs NH₂($\nu_2'' = 1$) + M (He, Ne, Ar, Kr).

have also been suggested for the vibrational relaxations of CH₄ [25] and HCO [26] by heavier inert gases. If several quanta of rotational energy are transferred from the vibrational bending mode of NH₂, induced by rare gas collisions, then the defect of vibrational energy transferred into translation will be significantly less [27]. If such is the case, either SSH theory based on repulsive intermolecular potentials [23] or Sharma's near-resonant model [28] based on the assumption of long-range attractive forces would explain the increase of the relaxation probability from Ne to Kr.

3.2. NH₂($\nu_2'' = 1$) + H₂, D₂

The observed decay rates of NH₂($\nu_2'' = 1$) with H₂ and D₂ respectively are displayed in fig. 4. The data were fit by a $k_{\text{obs}} = k_0 + k_r P_M$ linear least-squares program and plotted in the form of $k_{\text{obs}} - k_0$ versus P_M , where P_M is the pressure of the collision partners H₂ or D₂. In the analysis to follow, the reaction NH₂ + H₂ → NH₃ + H can be ruled out due to the enormous amount of energy required [7]. Therefore, the major decay channel will be vibrational relaxation of NH₂($\nu_2'' = 1$) by H₂ and D₂, respectively. The probabilities for energy transfer are also listed in table 1. The ratio $P(\text{H}_2)/P(\text{D}_2) \approx 2$ indicates that the collision partner H₂ is about twice as efficient as D₂ in relaxing NH₂($\nu_2'' = 1$). Similar results have been found for the deactivation of CH₄ [25] and CH₃Cl [23] by H₂ and D₂. The possible explanations for this observation are V-T, V-R, or both. Intermolecular V-V processes are expected to be negligibly small due to the very large negative energy defects,



The larger deactivation probability for NH₂($\nu_2'' = 1$) + H₂ with the larger energy defect ($\Delta E = 2823 \text{ cm}^{-1}$) also confirms this conclusion, since V-V processes are very sensitively and negatively dependent on the energy defect transferred into translational degrees of freedom. H₂ has both larger translational and rotational velocities than

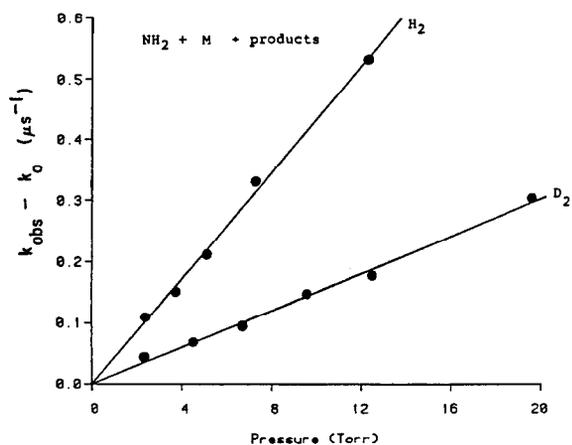


Fig. 4. As in fig. 2, but for the decay of NH₂(*v*''=1) through collisions with H₂ and D₂. The plot is in the form of $k_{\text{obs}} - k_0$ versus P_M , where k_{obs} is a pseudo-first-order observed rate constant, k_0 is the intercept of the least-squares linear fit of the experimental data, and P_M is the pressure of the collision partners, H₂ and D₂.

does D₂. These two factors both favor the enhancement of the relaxation rate of the collision pair NH₂(*v*''=1) + H₂, if V-R and V-T are dominant processes.

3.3. NH₂(*v*''=1) + N₂, CO, O₂

Comparisons of the decay rates and relaxation probabilities for NH₂(*v*''=1) + M(N₂, CO, O₂) are plotted in fig. 5 and listed in table 1.

In the case of NH₂ decay by collisions with O₂, the possibility of a competitive chemical reaction must also be considered. One such process,



has been proposed by Hack et al. [29] and other groups [30,31] as a major process in the reaction of NH₂ and O₂. However, the rate constant expression derived for this process [30] leads to decay rates much slower than the experimental values obtained in this study. The measured decay rate of NH₂, even at the highest pressure of O₂ used in this work (≈ 10 Torr), was much faster than the calculated rate, $k_{\text{O}_2} = 3.3 \times 10^4 \text{ s}^{-1}$. The negative temperature effect for this reaction [29] also suggests that the vibrational excitation of NH₂ would probably retard the reaction rate (9). The linear

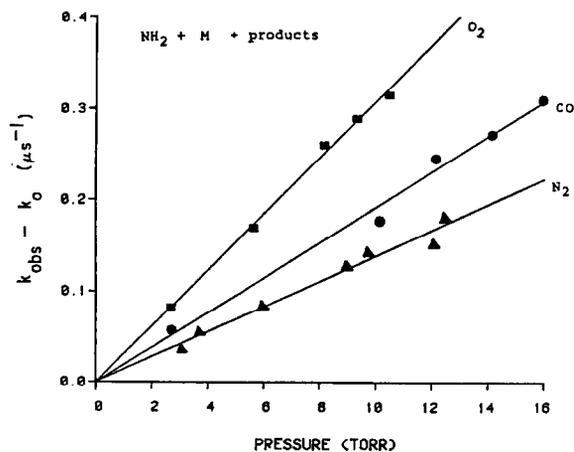


Fig. 5. As in fig. 4, but for decay of NH₂(*v*''=1) through collisions with N₂, CO, O₂.

dependence of the observed rate constant on O₂ pressure, as shown in fig. 5, also rules out reaction (9) as a major contributor to k_{obs} , since, the reaction would be third-order.

In addition, studies performed in this laboratory [7] on recombination reactions of NH₂(*v*''=0) radicals, showed that the main role of O₂ in these processes is that of a third-body collision partner for the reaction



Evidence in favor of this channel is given by the inverse power rate law observed for ground vibrational state NH₂(*v*''=0). This rate law is consistent with a second-order reaction such as (10), but inconsistent with the pseudo-first-order temporal behavior that is observed in these experiments with NH₂(*v*''=1).

These observations seem to indicate that chemical reaction is, if at all, of very minor importance in these studies. The same temporal behavior was observed for N₂ and CO.

As mentioned above, for the deactivation of NH₂(*v*''=1), V-R energy transfer can be expected to play an important role, if the reduced mass of the collision pairs is not very small. In the case where both collision partners (NH₂-M) are rotators, the one with the smaller moment of inertia (NH₂) is rotationally involved in V-R processes. It has been suggested [32] that for the

non-resonant $V-V \rightarrow T$ processes, short-range repulsive forces are more effective in inducing vibrational transitions, whereas for near resonant $V-V \rightarrow T$ processes, relatively weak long-range attractive forces are more important. The ratio $P(\text{CO})/P(\text{N}_2) = 1.4$, which indicates that CO is a more effective collision partner than N_2 , can be rationalized either by the smaller vibrational energy defect, $\Delta E = 660 \text{ cm}^{-1}$ in $\text{NH}_2(v_2'' = 1) + \text{CO}$ compared to $\Delta E = 848 \text{ cm}^{-1}$ in $\text{NH}_2(v_2'' = 1) + \text{N}_2$, or, where efficient $V-R$ occurs, by the stronger long-range intermolecular attractive forces between NH_2 and CO than that between NH_2 and N_2 (for dipole-dipole interaction, $\mu_{\text{CO}} = 0.10 \text{ D}$, $\mu_{\text{N}_2} = 0$; for dipole-induced dipole interaction $\alpha_{\text{CO}} = 1.95 \times 10^{-24} \text{ cm}^3$, $\alpha_{\text{N}_2} = 1.76 \times 10^{-24} \text{ cm}^3$, where α is the polarizability). A similar result for the $V-V$ deactivation of HCl by CO and N_2 respectively [33] showed that $P(\text{CO})/P(\text{N}_2) \approx 1.8$, even though $V-V$ relaxation of HCl by CO has a larger vibrational energy defect, $\Delta E = 743 \text{ cm}^{-1}$, than that of the HCl- N_2 collision pair, $\Delta E = 555 \text{ cm}^{-1}$. These results suggest the latter explanation may be more reasonable and the involvement of the rotation of NH_2 in the relaxation of the vibrational excitation will decrease the vibrational energy defect. As suggested by Seoudi et al. [34] for the H_nX ($n = 1, 2, 3, \dots$) type molecules, long-range multipolar interactions play a more important role in $V-V \rightarrow R, T$ processes, owing to the rapid rotational velocity of the hydrogen atom. This suggestion is further supported [35] by the decrease of the self-deactivation rate of $\text{H}_2\text{O}(v_2)$ caused by deuteration.

The most efficient collision partner studied is O_2 , $P(\text{O}_2) = 3.71 \times 10^{-3}$. This result is rationalized by the very small vibrational energy defect in the $V-V \rightarrow R, T$ process, $\Delta E = 59 \text{ cm}^{-1}$. This small energy gap can be further lessened by transferring a single quantum of the rotational energy into the specific rotational principal c axis of NH_2 , which has a rotational constant $C = 8 \text{ cm}^{-1}$ [36]. The most populated c -axis rotational quantum state, J_c , can be derived from the Boltzmann distribution expression, $J_{\text{max}} = 0.59 [T(\text{K})/C(\text{cm}^{-1})]^{1/2}$, which gives $J_c \approx 4$. The energy spacing between J_{max} and $J_{\text{max}} - 1$ is $\approx 64 \text{ cm}^{-1}$. Consequently, one quantum of the rotational en-

ergy transferred will decrease the extra vibrational energy which goes into translational degrees of freedom to 5 cm^{-1} . A similar case, $\text{CO}_2(001) + {}^{15}\text{N}_2(0) \rightarrow \text{CO}_2(000) + {}^{15}\text{N}_2(1) + 97 \text{ cm}^{-1}$ has been analyzed theoretically using first-order perturbation theory by Sharma and co-workers [37]. It was shown that only those rotational transitions which reduce the energy mismatch at $\omega\tau \leq 2$ are highly effective in causing vibrational energy transfer; where $\omega \equiv \Delta E/h$ is the Bohr frequency of the transition, ΔE is the energy mismatch, and $\tau \equiv b/\nu$ is the effective "time of interaction".

3.4. $\text{NH}_2(v_2'' = 1) + \text{CH}_3\text{NH}_2$

The total decay rate of $\text{NH}_2(v_2'' = 1)$ as a function of precursor CH_3NH_2 pressure over the range 30–120 mTorr is shown in fig. 6. The second-order decay rate constant obtained is $(8.43 \pm 0.53) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is only a factor of 3 lower than the gas kinetic rate constant.

The observed removal rate of $\text{NH}_2(v_2'' = 1)$ by CH_3NH_2 is two orders of magnitude larger than the observed removal rate constants in the presence of the mono- and diatomic collision partners. The likely cause is the increased number of vibrational degrees of freedom, some of which are vibrationally resonant with $\text{NH}_2(v_2'' = 1)$. Recently, further research work from our laboratory [9] strongly suggests that the vibrational relaxation of $\text{NH}_2(v_2'' = 1)$, due to collisions with CH_3NH_2 , is the major contributor to the total decay rate.

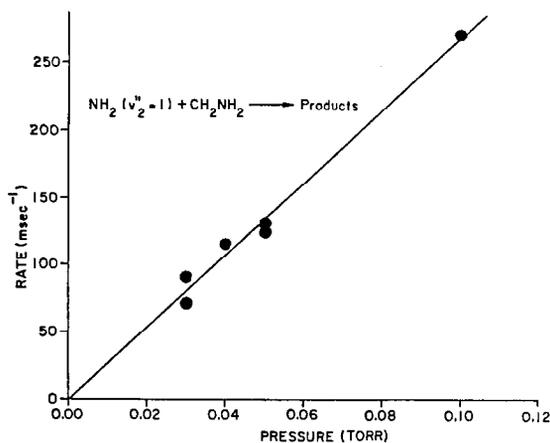


Fig. 6. As in fig. 2, but for decay of $\text{NH}_2(v_2'' = 1)$ through collisions with CH_3NH_2 .

5. Conclusion

From the above analysis, we see that our results can be qualitatively understood from different theoretical models, in which long-range multipolar forces are assumed. Very recently, Seoudi et al. [38] have used the semiclassical method of Dillon and Stephenson [17] to treat systems such as HX–N₂ or HX–N₂O, in which a dipole–quadrupole vibrational interaction or a dipole–dipole rotational interaction is assumed. Their calculations definitively showed the importance of long-range forces in enhancing the vibrational relaxation processes. At this stage, it is necessary for us to consider the vibrational relaxation of NH₂($v_2'' = 1$) + M in more theoretical detail. We plan to apply a modified form of Dillon's model to the NH₂–M system in order to understand the detailed nature of this process.

Acknowledgement

We gratefully acknowledge support of this work by the Department of Energy through Contract No. DE-AC02-78ER04695 Mod. 005 and the National Science Foundation through Grant No. CHE-8023362 for the equipment used in this study.

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