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David H. Mordaunt, Richard N. Dixon, and Michael N. R. Ashfold

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Photodissociation dynamics of *A* state ammonia molecules. II. The isotopic dependence for partially and fully deuterated isotopomers

David H. Mordaunt,^{a)} Richard N. Dixon, and Michael N. R. Ashfold School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

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The technique of H(D) Rydberg atom photofragment translational spectroscopy has been used to investigate the photodissociation dynamics of the mixed isotopomers NH₂D and NHD₂ following the excitation to the $v'_2 = 0$ and 1 levels of their lowest lying $\widetilde{A}^{-1}B_1(C_{2v})$ excited electronic states. Peaks in the resulting total kinetic energy release (TKER) spectra are assigned to levels of the NH₂, NHD, or ND₂ fragments with a wide range of quantum numbers K_a for rotation about their a inertial axes, and with $N = K_a$, $N = K_a + 1$, or $N = K_a + 2$ as appropriate. These data provide the first measurements of high rotational levels for the ground electronic state of the NHD radical. The least squares fitting of all these spectra, and those resulting from NH₃ and ND₃, to the best calculated NH₂, NHD, and/or ND₂ rotational term values provides accurate estimations of the respective N-H and N-D bond dissociation energies D_0^0 across the whole series. These values are $D_0^0(\text{H-NH}_2) = 37\ 115\pm20\ \text{cm}^{-1}\ (4.602\pm0.002\ \text{eV});$ $D_0^0(\text{H-NHD}) = 37\ 240\pm50$ cm^{-1} ; $D_0^{\bar{0}}(\text{H}-\text{ND}_2)=37\ 300\pm30\ \text{cm}^{-1};\ D_0^{0}(\text{D}-\text{NHD})=37\ 880\pm60\ \text{cm}^{-1};\ \text{and}\ D_0^{0}(\text{D}-\text{ND}_2)=38\ 010\pm20$ cm^{-1} . The differences between these values are fully consistent with differences in zero-point energies and lead to a mean value of $D_e = 40510 \pm 25$ cm⁻¹. Dissociation of NH₂D or NHD₂ through their (A - X) 2¹₀ bands to give an NHD product leads to TKER spectra with a much higher statistical character than those leading to an NH₂ or ND₂ product, and to those obtained following excitation through the 0_0^0 bands. This is rationalized in a semiquantitative manner in terms of a varying contribution to the dissociation rate of the parent molecules from internal conversion (IC) to high levels of their respective ground states. Nuclear permutation symmetry appears to play an important role both for the IC rates and for the subsequent branching between product channels. © 1996 American Institute of Physics. [S0021-9606(96)01715-7]

I. INTRODUCTION

The photochemistry of polyatomic hydride molecules has been shown to involve a wide variety of dissociation mechanisms. H₂O excited to its $\overline{A}^{-1}B_{1}$ electronic state within a region of continuous absorption centered about 165 nm dissociates directly to give H+OH(X $^{2}\Pi$) ground state products.¹ The distribution of the available energy over the rotational and Λ -doublet states of OH is highly specific, and is interpreted in terms of tight dynamical constraints during the process of dissociation which takes place on a single potential energy surface. In contrast, when CH₄ is photolyzed within its first absorption continuum at 121.6 nm the H+CH₃ product state internal energy distribution appears to be purely statistical.² The lowest dissociation energy is to $H+CH_3(\tilde{X}^2A_1)$, although at higher internal energy of the fragments there is competition between a number of open dissociation channels. In this case the potential energy surface for the $CH_4(\tilde{A}^{-1}T_2)$ excited state does not correlate directly with the H+CH₃ ground state products, and dissociation is thought to be initiated through internal conversion to high vibrational levels of the CH₄ ground state. Both of these cases involve excitation through absorption continua.

The first excited states of NH_3 (Refs. 3–6) and the methyl radical (Refs. 7 and 8), and higher excited states of H_2O (Refs. 9-11), all give rise to structured regions of absorption indicating longer-lived excited electronic states and illustrate further dissociation mechanisms. In CH₃ and in NH₃ (both of which have electronic origins near 216 nm), there is a barrier on the first excited state surface between an inner well and the dissociation channel, and predissociation from the lowest excited quasibound levels proceeds by quantum tunneling through this barrier. For higher vibrational levels of $NH_3(A)$ intramolecular vibrational redistribution (IVR) converts energy in a vibrational coordinate orthogonal to the dissociation path into motion along this path, so that quantum tunneling is no longer necessary. The consequence is a much shortened excited state lifetime. Even so, for NH₃ in its first excited state, and for H₂O molecules in their second excited state, the dissociation dynamics are dominated by strong forces acting in the exit channel, brought about by a conical intersection of two potential energy surfaces.

The accompanying paper¹² (hereafter referred to as paper I) summarizes current knowledge of the photochemistry of ammonia, and describes improved experiments concerning the dissociation dynamics of NH₃ and ND₃ excited to either the origin level, or the 2¹ vibrational level, of their $A \sim {}^{1}A_{2}''$ excited states. These experiments reveal a dramatic correlation between the fragment recoil velocity vectors and the *a*-axis rotational angular momentum of the NH₂(ND₂) fragment.

The tunneling rate for breaking an N–D bond is an order

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^{a)}Present address: Department of Chemistry, University of California, Berkeley, CA 94720, USA.

of magnitude slower than that for an N–H bond. One might therefore predict that in partially deuterated ammonias an NH bond would break in preference to an ND bond, and that the dynamical properties would be intermediate between those of NH_3 and of ND_3 .

This paper presents new high resolution experimental measurements of the internal energy distribution of the fragments of dissociation of NH2D and NHD2 following excitation to excited levels with $v'_2 = 0$ or 1. We find that in all four cases the branching ratio does indeed favor the breaking of an NH bond, but also that this ratio varies widely across the series. Comparison of these branching ratios and absorption linewidth measurements suggests that, in addition to the dynamical dissociation controlled by quantum tunneling, there is a competing statistical dissociation mechanism. Furthermore, the spectra of the total kinetic energy release (TKER) of the mixed isotopomers are not intermediate in character between those of NH₃ and of ND₃. In the most extreme case, that of $[NHD_2(2_0^1) \rightarrow D + NHD]$, the internal energy distribution has a dominant statistical character, whereas the competing and more favored $[NHD_2(2_0^1) \rightarrow H + ND_2]$ channel has a much higher dynamical character. These various observations are rationalised in terms of a varying contribution to the overall dissociation rate from an initial internal conversion to high levels of the parent molecular ground state. Nuclear permutation symmetry appears to play a significant role in controlling both this rate and the subsequent dissociation, giving the highest statistical character for a mixed isotopomer dissociating to give the unsymmetrical NHD product.

II. EXPERIMENT

The photofragment spectrometer has been described in detail in previous publications, and is summarized in paper $I.^{12}$ Briefly, a skimmed pulsed supersonic beam of NH₃ and ND₃ (in equimolar proportions)-typically seeded as a 1% mixture in argon—is intercepted at right angles by three pulsed laser beams to initiate photolysis and "tag" the nascent H or D atomic fragments. The photolysis photons are generated by third harmonic generation from a tuneable dye laser operating on the dye DCM. The electric vector of this 3ω radiation could be rotated relative to the atomic flight axis. The times-of-flight to a detector of these tagged "Rydberg atoms" are recorded and transformed to a recoil kinetic energy distribution. As in paper I, the energy resolution of these total kinetic energy release spectra was improved over that of earlier studies of NH₃ and ND₃ photolysis⁴⁻⁶ by the use of a longer flight path of 825.6 mm from the interaction region to a grounded mesh immediately before the front face of the detector.

Both H and D atoms were probed, and for the mixed isotopomers it was important to measure the branching ratios between these two dissociation channels. The shift between the excitation wavelengths for H and D atoms is sufficiently small that there was no difficulty in switching between these. Even so, in order to normalize the two spectra thus generated, it was not only necessary to hold conditions stable across both experiments, but also to take into account the FIG. 1. Total kinetic energy release (TKER) spectra, all plotted on a common energy scale, for the $H/D+NH_xD_{2-x}$ fragments resulting from photolysis of jet-cooled samples of the various isotopomers of ammonia excited within the 0_0^0 bands of their $\widetilde{A}-\widetilde{X}$ transitions, and with $\epsilon_{\rm phot}$ aligned first parallel, and then perpendicular, to the TOF axis.

differing sampling of the Doppler widths of the H/D atomic transitions. This difference arises from the mass dependence of the momentum balance for the kinetic energy release, since the Doppler widths were greater than the laser bandwidth.

Under conditions of jet cooling, the 0_0^0 and 2_0^1 bands of the $\widetilde{A} - \widetilde{X}$ electronic band systems of all of the isotopomers—NH₃, NH₂D, NHD₂, and ND₃—are essentially free from overlapping, as is discussed in connection with band simulations described later. Spectra were recorded for excitation at chosen frequencies within all eight of these bands. Both H atoms and D atoms were sought whenever expected, but the D atom flux from NH₂D was sufficiently weak that a tolerable signal-to-noise ratio could only be obtained in perpendicular polarisation. Other than this, at least four spectra were recorded for each target molecule; for two polarizations and two frequencies, and an additional four for a second dissociation channel where appropriate.



III. BOND DISSOCIATION ENERGIES

It is clear from Fig. 1 that for excitation of NHD₂ via its 0_0^0 band the maximum total kinetic energy release for NHD₂ \rightarrow D+NHD is lower than that for NHD₂ \rightarrow H+ND₂. Thus the dissociation energy for the ND bond is higher than that for the NH bond. Similar comparisons can be made across the whole range of isotopomers after taking into account the differences in excitation energy. The potential energy surfaces for all these processes must be the same at the level of the Born–Oppenheimer approximation. These differences in zero-point energies between the parents and between the fragments.

It is necessary to know the ground state rotational energies for ND₂ and NHD before we can establish accurate values for all these dissociation energies. Biesner et al.⁵ reported experimentally fitted eigenvalues for the important range of levels of $NH_2(X)$ and $ND_2(X)$ from the TKER spectra from photolysis of NH₃ and ND₃, respectively. In striving for higher accuracy we use the term values for $NH_2(v_2, N=K_a)$ which have been derived by optical spectroscopy.¹³ Those experimental measurements had been analyzed by fitting them to the eigenvalues of a "semirigid bender Hamiltonian,"14 which includes Renner-Teller coupling between the $\tilde{A}^{2}A_{1}$ and $\tilde{X}^{2}B_{1}$ electronic states which correlate with a single ${}^{2}\Pi_{\mu}$ state of linear NH₂. The potential energy curves thus derived for the two component states incorporate the zero-point energies of the two stretching vibrations and compensate to some extent for the effects of stretch-bend interaction while the molecule rotates. This model calculation provides a good representation of the ground state levels of $v_2 = 0$ and 1 for all K_a and $N \approx K_a$. Substitution of the mass of D for that of H in these calculations then gave good initial estimates for the eigenvalues for the $X^{2}B_{1}$ state of ND₂. From this starting point it proved possible to assign the individual peaks in the TKER spectra for H or D atoms with an ND₂ partner. The resulting term values for ND_2 are reported in paper I.¹²

The use of this model is less straightforward for NHD because of the loss of C_{2v} symmetry. This causes a rotation of the principal inertial axes to allow for the imbalance of H and D. A simplification was therefore introduced which is reasonably valid for the rotational levels for $v_2=0$. The bending zero-point energy and other higher order terms were also incorporated into a suitably modified ground state bending potential energy curve. For the high rotational levels of interest K_a is a good quantum number. Consequently, for each required level this curve was augmented at every angular coordinate for the N- and K_a -dependent centrifugal energy in a symmetric-top principal axis coordinate system, and the eigenvalue estimated as the minimum of this effective potential. In this manner the experimental term values for NH₂($v_2=0$) could be reproduced to within $\pm 1 \text{ cm}^{-1}$. A good fit to the less precise data for ND₂ was obtained with slightly modified potential parameters. A starting point for the NHD calculations was then made by interpolating between these two sets of potential parameters and making the appropriate changes of mass and rotation of axes. On this



FIG. 2. Total kinetic energy release (TKER) spectrum for the D+NHD fragments resulting from the photolysis of NHD₂ at 46 529 cm⁻¹ with ϵ_{phot} aligned perpendicular to the TOF axis (see also Fig. 1). The combs above the spectrum indicate the assignments of peaks to levels of NHD with $v_2=0$, and with $N=K_a$, $N=K_a+1$, and $N=K_a+2$. The low K_a head for $v_2=1$ underlies these series near 7300 cm⁻¹.

basis it has proved possible to make unambiguous assignments of the TKER spectra for an NHD partner (Fig. 2) and, hence, to make a refined fit to the observations. An important feature of these assignments is the detection for NHD of far stronger peaks with $N > K_a$ than are observed for NH₂ or ND₂—a point to which we return later. The final calculated rotational term values for the ground vibrational level of NHD are given in the Appendix.

Given these accurate values for the term values for NH_2 , NHD, and ND_2 , least squares fits to the $v_2=0$ and low K_a portions of the various TKER spectra yield the values for the TKER appropriate to the $N=K_a=0$ levels of each ground state product. At the time that these experiments were carried out there were no detailed experimental assignments for the bands of the mixed $\text{NH}_x\text{D}_{3-x}$ parent isotopomers, and the TKER spectra were obtained by choosing excitation wave numbers within the 0_0^0 and 2_0^1 bands that maximized the H/D atom fluxes from our cold molecular beams. Very recently, Henck *et al.* have used microwave detected, microwave-



FIG. 3. Calculated absorption profiles for the 0_0^0 and 2_0^1 bands of the $\widetilde{A} - \widetilde{X}$ transitions of NH₂D and NHD₂ using a rotational temperature of 15 K, but a 300 K nuclear spin temperature. The dominant rovibronic transitions are indicated in each case. For consistency these are all given in an oblate top nomenclature $\Delta J_{Kc}(J)$, with $\Delta K_c = 0$ for all transitions. Spectroscopic constants and linewidth parameters are from MODR experiments (Ref. 15).

TABLE I. Excitation transitions and bond dissociation energies where measured.

Isotopomer	ν (cm ⁻¹)	Vibronic band	Principal transition(s)	$D_0^0 (N-H)/(cm^{-1})$	$D_0^0 (\text{N}-\text{D})/(\text{cm}^{-1})$
NH ₃	46 200	00	$R_0(1)$ and $R_1(1)$	37 115±20	
	47 069	2_0^1	$R_{0}(0)$		
NH_2D	46 359	00	$R_{1}(1)$	37 240±50	
-	47 155	2_{0}^{1}	$R_{0}(0)$		
NHD ₂	46 529	0 <mark>0</mark>	$R_{0}(0)$	37 300±30	37 880±60
	47 264	2_{0}^{1}	$R_{0}(0)$		
ND ₃	46 708	0 <u>0</u>	$Q_{1}(1)$		$38010{\pm}20$
	46 724	00	$R_{0}(0)$		
	47 362	$2_0^{\hat{1}}$	$Q_1(1)$		

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optical double resonance (MODR) to analyze excitation spectra for all the isotopomers.¹⁵ Figure 3 presents absorption spectra for the 0_0^0 and 2_0^1 bands of the mixed isotopomers calculated using their molecular parameters for our beam temperature of 15 K. Figure 3, together with Fig. 3 of Ref. 12 which presents equivalent calculated spectra for NH₃ and ND₃, demonstrates that at this beam temperature there is no significant overlap between the bands of the various isotopomers present in our mixed sample. We are thus able to deduce the precise parent molecule and excitation transitions for each of our TKER spectra, although lifetime broadening denies the possibility of excitation via a single rovibronic transition in most cases. The bond dissociation energies are then derived using

$$D_0^0(\mathrm{H-NH}_2) = E_{\mathrm{int}}(\mathrm{NH}_3) + h\nu$$

-TKER(H+NH₂)- $E_{\mathrm{int}}(\mathrm{NH}_2),$ (1)

and its corresponding isotopic variants for the other isotopomers. Fragment levels with $v_2=0$ and low values of N and K_a are substantially populated for excitation within the 0_0^0 bands, but much less so for the higher vibronic bands. The extrapolation from the observed peaks to zero internal energy is therefore minimized for the 0_0^0 bands, and these have been preferred for the measurement of the bond dissociation energies. Table I presents the dissociation energies thus derived for all the processes studied. Note that these span a range of almost 1000 cm⁻¹.

The photolysis laser wave numbers were calibrated to a precision of $\pm 0.5 \text{ cm}^{-1}$ in these experiments and in each case the mean internal energy of the parent molecule is less than 20 cm⁻¹. Some imprecision stems from the laboratory to center-of-mass energy Jacobian to allow for the parent beam velocity, estimated as $450\pm75 \text{ m s}^{-1}$. This shifts the observed TKER spectrum by about -9 cm^{-1} in the case of NH₃. The final best estimate of $D_0^0(\text{H}-\text{NH}_2)$ is 37 115±20 cm⁻¹ (4.602±0.002 eV), as reported in paper I. This value improves on the previous determination of 4.64(5) eV from the H⁺ ion time-of-flight (TOF) technique,⁴ and the currently recommended literature value of $4.635\pm0.003 \text{ eV}$.¹⁶

These various D_0^0 dissociation energies are related to the equilibrium dissociation energies D_e , which should be essentially isotopomer independent, through the differences in zero-point energy ($E_{\rm ZP}$). Thus, for NH₃,

$$D_e(H-NH_2) = D_0^0(H-NH_2) + E_{ZP}(NH_3) - E_{ZP}(NH_2).$$
(2)

The vibrations of NH_3 , NH_2 , and their isotopomers are noticeably anharmonic, and the zero-point energies are most accurately represented by including quadratic terms in the vibrational quantum numbers. For NH_3 and ND_3 ,

$$E_{\rm ZP}(NX_3) = 1/2 \sum_r \omega_r d_r + 1/4 \sum_{r \ge s} x_{rs} d_r d_s, \qquad (3)$$

in which the degeneracy factors d_r are equal to 1 for r=1 and 2, and 2 for r=3 and 4. For the less symmetric molecules,

$$E_{\rm ZP} = 1/2 \sum_{r} \omega_r + 1/4 \sum_{r \ge s} x_{rs}, \qquad (4)$$

where r=1-3 for NH₂, NHD, and ND₂; and r=1-6 for NH₂D and NHD₂. Unfortunately, NH₃ is the only one of these molecules for which all the necessary parameters have been derived from the analysis of spectroscopic data.¹⁷ However, high quality ab initio potential energy surfaces for ammonia¹⁸ and the amino radical¹⁹ have been used to calculate spectroscopic parameters for all their isotopomers. Table II lists all the harmonic ω_r values from these calculations, and the empirical values for NH3. The empirical zero-point energy for NH_3 calculated from Eq. (3) with the complete set of anharmonic parameters is 2.8% lower than that from the purely theoretical parameters. Comparisons of other ω_r values where available indicate similar errors in the ab initio values. Zero-point energies for the whole set of isotopomers have therefore been derived from the *ab initio* spectroscopic parameters by applying a consistent reduction by 2.8%. The values of D_e thus obtained from the five experimental values of D_0^0 are in excellent agreement with one another (Table III) and lead to a mean value of $D_e(H-NH_2)=40510\pm25$ cm⁻¹.

IV. PRODUCT STATE POPULATION DISTRIBUTIONS

TKER spectra have been recorded for dissociation of all the NH_xD_{3-x} isotopomers through selected excitations within their 0_0^0 and 2_0^1 bands (Table I). In each case measurements have been made with the time-of-flight path both parallel and perpendicular to the electric vector of the dissociation laser and, additionally, at intermediate angles in some

TABLE II. Harmonic vibration frequencies for the \widetilde{X} states of the H/D isotopomers of ammonia and the amino radical.

	Mode					
Molecule	$\omega_1 \ (\mathrm{cm}^{-1})$	$\omega_2 \ (\mathrm{cm}^{-1})$	$\omega_3 \ (\mathrm{cm}^{-1})$	$\omega_4 \ (\mathrm{cm}^{-1})$	$\omega_5 (\mathrm{cm}^{-1})$	$\omega_6 \ (\mathrm{cm}^{-1})$
NH ₃ ^a	3503	1030	3592	1690		
NH3 ^b	3546	1141	3687	1733		
NH_2D^b	3598	2649	1699	1052	3687	1478
$\rm NHD_2^{b}$	3644	2590	1318	952	2712	1550
$ND_3^{\overline{b}}$	2534	867	2712	1258		
$\rm NH_2^{c}$	3374	1524	3481			
NHD ^c	2498	1337	3430			
ND ₂ ^c	2440	1119	2561			

^aEmpirical fit to spectroscopic data (Ref. 17).

^bFrom *ab initio* calculations (Ref. 18).

^cFrom *ab initio* calculations (Ref. 19).

cases. Many of these spectra exhibit a significant anisotropy: this is discussed in detail in paper I. We merely note here that the integral product state distributions can be obtained as a weighted mean of the measurements at 0° and 90° .

A. Dissociation through the 0⁰₀ bands

The dissociation dynamics of NH_3 excited via its 0_0^0 band has been amply discussed in previous publications.^{4-6,20} There is an almost uniform population of levels of NH₂ with $v_2=0$ and $N=K_a$, with N ranging from 0 to 20. A weaker series for $v_2=1$, $N=K_a$, and N=0-19 is also discernible, the low N head of which is responsible for an underlying broad peak in each spectrum of Fig. 1, as are two short series for $v_2=0$ and 1, with $N=K_a+1$. The source of this rotational excitation derives from the zero-point energies of the two disappearing bending vibrations of NH₃: ν'_2 correlates with rotation of NH_2 about its *a* rotational axis; whereas the $b_2(C_{2\nu})$ component of ν'_4 correlates with rotation about its c axis. A conical intersection in the exit channel between the Aand \widetilde{X} potential energy surfaces of NH₃ has a dramatic influence on the first of these, providing strong acceleration of the out-of-plane bending motion which results in excitation of a wide range of K_a states. In contrast, there are no strong forces to cause such an acceleration for the c axis rotation. The observation that levels with $N > K_a$ are weak and mainly at low K_a can thus be understood by noting that for levels with $N = K_a + 1$ the *c*-axis component of the rotational energy increases proportionally to (K_a+1) . Furthermore, the \angle HNH angle at the transition state between the quasibound inner well of NH₃ and the exit channel ($\sim 110^{\circ}$) is not greatly different from the equilibrium value for the ground state of NH₂ (105°); hence the predominance of levels with v_2 (NH₂)=0.

The dissociation of ND₃ through its 0_0^0 band has previously been studied using D⁺ ion TOF spectroscopy, but the resolution was inadequate for all but the coarsest rotational structure.⁵ Here we report much higher resolution spectra (paper I, and also Fig. 1). The energy disposal is very similar to that for NH₃. The predominant peaks are again those for population of the $v_2=0$, $N=K_a$ levels of ND₂, with weaker series for $v_2=0$, $N=K_a+1$ and $v_2=1$, $N=K_a$. This has allowed us to derive term values (and confirm our calculated values) for these previously unobserved levels of ND₂(\tilde{X} ²B₁) (see paper I).

We now turn our attention to the mixed isotopic parent molecules NH₂D and NHD₂. For NH₂D \rightarrow D+NH₂, and for NHD₂ \rightarrow H+ND₂, the fragmentation patterns are very similar to those for NH₃ and ND₃, respectively, with the same dominant series of peaks. These are the processes for which the breaking bond is parallel to the C_2 axis of the molecular fragment. In contrast, although the peaks in the spectra for NH₂D \rightarrow H+NHD and NHD₂ \rightarrow D+NHD may be assigned in the same way, principally to levels with $v_2=0$, their relative intensities differ substantially from those described above but are similar to each other (Figs. 1 and 2). For low values of K_a the strongest peaks are for $N=K_a$, but above $K_a=6$ the strongest peaks become those with $N=K_a+1$, and those with $N=K_a+2$ are almost as strong. The interpretation of this observation lies in the lack of C_2 symmetry during the

TABLE III. Zero-point energies and equilibrium bond-dissociation energies D_e for the isotopomers of ammonia.

NH2 37 115 ND2 38 010 ND2 37 300 NHD 37 880	7415400540 5255467293840 5396117293840 4796117350640 491	
NH2 37 115 ND2 38 010 ND2 37 300 NHD 37 880 NHD 37 240	7415 4005 5467 2938 6117 2938 6117 3506 6785 3506	40 525 40 539 40 479 40 491 40 519

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FIG. 4. Total kinetic energy release (TKER) spectra for the $H/D+NH_xD_{2-x}$ fragments resulting from photolysis of jet-cooled samples of the various isotopomers of ammonia excited within the 2_0^1 bands of their $\widetilde{A}-\widetilde{X}$ transitions, and with ϵ_{phot} aligned first parallel, and then perpendicular, to the TOF axis. The sharp spikes for *all* these spectra are genuine and repeatable peaks, not noise.

bond breaking process. The forces acting at the conical intersection remain in the plane bisecting the \angle HND angle, but the *a*-inertial axis of the NHD fragment now makes an angle of about 21° to the perpendicular to this plane. Consequently, the angular momentum generated by this force not only has a major component along *a* axis of NHD, but also has a significant component along the *b* axis.

The aforementioned discussion is concerned with the resolved rotational structure in each of the TKER spectra. It may be noted (Fig. 1) that many of these spectra also exhibit a weak underlying continuum, particularly for low kinetic energy release. We shall see that this is a more prominent feature for dissociation via the 2_0^1 bands.

B. Dissociation through the 2¹₀ bands

We have previously observed that when NH₃ or ND₃ is dissociated through excitation to higher members of the \tilde{A} - $X ~ 2_0^n$ progression the rotational population distribution of the fragment becomes strongly inverted, and there is an increasing excitation of the bending vibration of the fragment. Nevertheless, although there is little population of the low rotational levels for excitation through the 2_0^1 bands (Fig. 4), the important series of levels are again those with $N \approx K_a$.^{4,5} This was rationalized by considering the form of the respective out-of-plane vibrational wave functions of the parent molecule: that for $v'_2 = 0$ favors dissociation from near-planar geometries, whereas that for $v'_2 = 1$ has a node which discriminates against near-planar dissociation and low resultant angular momentum.

The TKER spectrum for $NHD_2 \rightarrow H + ND_2$ has a very similar intensity distribution to that for $ND_3 \rightarrow D + ND_2$, with the same prominent rotational series (Fig. 4): there is an equivalent $NH_2D \rightarrow D + NH_2$ comparison for and $NH_3 \rightarrow H + NH_2$, although all these spectra show a more prominent background continuum than for dissociation via the 0_0^0 bands. These processes all preserve $C_{2\nu}$ symmetry. The situation is strikingly different where NHD is the molecular fragment. It is still possible to assign peaks to the series of levels with $N \approx K_a$ for NH₂D \rightarrow H+NHD, although there are many other unassigned peaks and a substantial con-However, in the case tinuous background. $NHD_2 \rightarrow D + NHD$ the continuum is dominant and few peaks can be assigned with any certainty. This continuum is strongest at low kinetic energy release, corresponding to high NHD internal energy. This is qualitatively what would be expected for a statistical distribution over the vibrational and rotational degrees of freedom of NHD, rather than the dynamical population of a specific sub set of levels as in the more symmetrical molecules. A clue to this variable behavior is to be found in the pattern of H/D branching ratios for the mixed isotopomers.

V. ISOTOPIC BRANCHING RATIOS

The branching ratios for the production of H and of D atoms from the mixed isotopomers should provide further detailed evidence concerning the dissociation mechanism. Several experiments were therefore carried out under carefully controlled conditions to establish absolute branching ratios.

For each TOF spectrum the total atom flux was obtained by summation over the complete spectrum. The flux is, in general, anisotropic as is evident from Figs. 1 and 4. This anisotropy, and its variation with the excitation transition and the associated product states, is discussed in detail in paper I. For the purposes of measuring branching ratios the consequences of this anisotropy were eliminated by taking the weighted mean intensity as $(I_{\parallel} + 2I_{\perp})/3$. Furthermore, since it had not proved feasible to measure the ratio of I_{\parallel} to I_{\perp} in all cases, the reasonable assumption was made where necessary that this polarization ratio was the same for the corresponding H and D channels. The measurements are summarized in Table IV which also includes the homogeneous linewidths [full width at half maximum (FWHM)] recently measured by MODR.¹⁵

The dynamics of dissociation through excitation within the 0_0^0 and 2_0^1 bands of NH₃ and ND₃ has been attributed to quantum tunneling through any one of three equivalent exit-

	H channel	D channel		H:D ratio	Γ (cm ⁻¹)	
Isotopomer 0°:90°		0°:90° 0°		90°	Weighted mean	FWHM Ref. 15
0_0^0 band						
NH ₃	0.62 ± 0.03		∞	∞	∞	34.0 ± 0.8
NH ₂ D	0.65 ± 0.05	nm	nm	33±9	32 ± 9	34.0 ± 1.8
NHD ₂	0.62 ± 0.06	$0.70 {\pm} 0.09$	10 ± 2	12±3	11 ± 2	20 ± 2
ND ₃		$0.54 {\pm} 0.04$	0	0	0	4.2 ± 0.2
2_0^1 band						
NH ₃	1.16 ± 0.07		∞	∞	∞	29.2 ± 0.6
NH ₂ D	$1.18 {\pm} 0.07$	nm	nm	21 ± 4	20 ± 4	23.0 ± 0.6
NHD ₂	1.08 ± 0.09	1.19 ± 0.10	3.0 ± 0.6	3.6 ± 0.7	3.3 ± 0.7	12.8 ± 0.6
ND ₃		0.99 ± 0.02	0	0	0	1.5 ± 0.1

TABLE IV. Total H and D atom flux ratios from photolysis of isotopomers of ammonia. nm represents not measured.

channel barriers. The various linewidths for these excited states have also been shown to be in reasonable quantitative accord with this assumption, albeit with a barrier height rather lower than the currently available *ab initio* value.^{21,22} To a first approximation it might be expected that there would be a characteristic tunneling rate for an N–H bond, and a lower value for an N–D bond. From the data of Table IV these elementary widths per bond for $v'_2 = 0$ are 11.3 cm⁻¹ for N–H and 1.4 cm⁻¹ for N–D, (a ratio of 8.1:1); and for $v'_2 = 1$ are 9.7 cm⁻¹ for N–H, and 0.5 cm⁻¹ for N–D (a ratio of 19.5:1). The lower widths and higher ratio for $v'_2 = 1$ have been attributed to an increase in the barrier height with departure from planarity.²³

Two conclusions would follow from this assumption of independent bond dynamics. Firstly, for the mixed isotopomers the linewidths should show a linear dependence on the number of D atoms. However, the linewidths for NH₂D and NHD₂ are substantially greater than predicted by interpolation between NH₃ and ND₃ for both $v'_2 = 0$ and 1. Secondly their H/D branching ratios should be related to the ratios of these line-widths. On this basis, and given the relative numbers of H and D atoms, the following values are predicted for the H/D ratios. Tunneling from 0^0_0 band excitation:

$$NH_2D H/D = 16.2; experiment = (32 \pm 9),$$
 (5)

NHD₂ H/D=4.0; experiment=
$$(11\pm 2)$$
. (6)

Tunneling from 2_0^1 band excitation:

NH₂D H/D=39.0; experiment= (20 ± 4) , (7)

NHD₂ H/D=9.7; experiment=
$$(3.3\pm0.7)$$
. (8)

Even though these predictions rest heavily on an assumption of pure tunneling for NH_3 and ND_3 , this simplistic model is clearly not adequate. Either the remaining vibrational coordinates make a cooperative contribution to the effective potential for tunneling, or there is a further contribution to the dissociation mechanism.

We now return to the observation of an apparent statistical contribution to the rovibrational population distribution for some of the product states. This definitely suggests the involvement of a large number of degrees of freedom. It is also instructive to note that for NHD₂ the continuum is much more in evidence for the channel to [D+NHD] in direct competition with that to $[H+ND_2]$, particularly for dissociation through the 2_0^1 band (Fig. 4). Furthermore, the presence of assignable structure on top of a smooth continuum also suggests that there are contributions from two independent mechanisms, even for the 0_0^0 excitation. The levels of the \widetilde{A} state are embedded in the continua of both the \widetilde{X} state and the \widetilde{a}^3A'' state, coupling to either of which could provide additional routes to dissociation.

A. Dissociation initiated through internal conversion

The \tilde{a} -state surface has been calculated to lie less than 0.5 eV below that for the \tilde{A} state, with a very similar potential function apart from a much lower barrier in the exit channel, and no strong coupling where it crosses the \tilde{X} -state surface.²⁴ It is therefore doubtful that it would have a sufficient density of states to permit efficient intersystem crossing (ISC). Furthermore, any such ISC would be unlikely to lead to a fully statistical product state energy disposal. On the other hand, the densities of vibrational levels of the \tilde{X} states at the energy of the \tilde{A} -state origins, calculated in the harmonic approximation (which surely gives an underestimate), are about 40/cm⁻¹ for NH₃ and 200/cm⁻¹ for ND₃ which are high enough to facilitate internal conversion (IC).

The most probable additional mechanism is therefore internal conversion to high-lying levels of the molecular ground states, but with a rate relative to tunnelling which is quite state specific. The IC rates in each molecule should increase with increasing v'_2 since this mode transforms as the direct product of $\widetilde{A} \times \widetilde{X}$, but the variation across the isotopomer series will depend on the interplay between an increasing density of states and a decreasing coupling matrix element. There is, however, an additional factor that must be taken into account; the subdivision of the densities of states to allow for nuclear permutation symmetry, which is probably the only relevant symmetry for very high levels of the \widetilde{X} states. For NH₃ and ND₃, the permutation symmetry group π_3 is isomorphous with D_3 , and the density can be subdivided into $[\frac{1}{6} \times A_1 + \frac{1}{6} \times A_2 + \frac{2}{3} \times E]$. For NH₂D and NHD₂, the group is π_2 , isomorphous with C_2 , and the division is $[\frac{1}{2} \times A + \frac{1}{2} \times B]$. Since, in all cases, the parent rotational angular momentum is very low (J' = 1 or 2, Table I), and the coupling is almost certainly vibronic, we consider only the vibronic symmetry of the initially excited levels. These are either $A_2(v'_2 = 0)$ or $A_1(v'_2 = 1)$ for NH₃ and for ND₃, and A for both vibrational states of NH₂D and NHD₂. Since permutation symmetry must be conserved in IC, the accessible fraction of the density of states is only one-sixth of the total for NH₃ and ND₃ and one-half for NH₂D and NHD₂. This provides a plausible explanation for the increased background continuum for the mixed isotopomers, particularly for $v'_2 = 1$.

We now consider the branching between product channels from a highly excited ground state level for the mixed isotopomers. There is no barrier to hinder such a process, so the dissociation will take place through a loose transition state. The rates can therefore be calculated by unimolecular decay theory and will depend on the total densities of states for the highly rotating and vibrating bent triatomic molecular product, together with the three-dimensional partition function for the translational recoil of the H/D atom. For a given parent molecule and energy the *ratio* of these branching rates can be calculated from purely geometrical and mass factors. The vibrational density is proportional to $[\det G]^{-1/2}$, the rotational density to $[\det I]^{1/2}$, and the translational density to $\mu^{1/2}$. This leads to total statistical ratios of [1.88:1] for $[NH_2D \rightarrow H + NHD]:[NH_2D \rightarrow D + NH_2]$, and [1.89:1] for $[NHD_2 \rightarrow H + ND_2]: [NHD_2 \rightarrow D + NHD].$

For both parent molecules the NHD product can be formed by the breaking of either of two bonds, and there is no nuclear permutation restriction. However, there is only one route to yield either NH_2 or ND_2 , and only one-half of the product states have the same nuclear permutation symmetry as any one parent state. The overall calculated branching ratios between the two pairs of channels are as follows. Internal conversion:

$$[\mathrm{NH}_{2}\mathrm{D} \rightarrow \mathrm{H} + \mathrm{NH}\mathrm{D}]:[\mathrm{NH}_{2}\mathrm{D} \rightarrow \mathrm{D} + \mathrm{NH}_{2}] = [7.5:1], \quad (9)$$

$$[\mathrm{NHD}_2 \rightarrow \mathrm{H} + \mathrm{ND}_2]: [\mathrm{NHD}_2 \rightarrow \mathrm{D} + \mathrm{NHD}] = [0.47:1]. (10)$$

On this basis the greatest contributions of internal conversion to the overall dissociation rate across the whole series of isotopomers should be for $[NH_2D\rightarrow H+NHD]$ and for $[NHD_2\rightarrow D+NHD]$. These are precisely the processes for which the TKER spectra have the highest proportion of background continuum for $v'_2 = 1$, and to a lesser extent for $v'_2 = 0$. Figure 5 compares the TKER spectrum for the $[NHD_2(2_0^1)\rightarrow D+NHD]$ dissociation with a statistical distribution based on a harmonic oscillator+rigid rotor density of states for the three vibrational and three rotational degrees of freedom of NHD and the relative translation of D. This gives a faithful reproduction of the continuum underlying the resolved structure and it is thus clear that IC provides the dominant decay route for this process.

FIG. 5. The total kinetic energy release (TKER) spectrum of the D+NHD fragments resulting from photolysis of NHD₂ at 47 264 cm⁻¹ (see also Fig. 4). The smooth curve is calculated for a statistical distribution over all the yibrational, rotational and translational degrees of freedom of the fragments, representing dissociation following internal conversion to high levels of the parent molecular ground state. This has been scaled to indicate how the total

flux might be made up from this smoothly varying internal conversion con-

tribution and a structured contribution from tunneling.

Let us now use the H/D branching ratios to assess the relative rates from tunneling (k_{TUN}) and internal conversion $(k_{\rm IC})$ following 2_0^1 band excitation. Note that the experimental ratios for both pairs of isotopomer dissociation processes are intermediate between the statistical values of Eqs. (9) and (10) and the purely tunneling values of Eqs. (7) and (8). For NHD₂, the experimental H/D ratio can be reproduced using a ratio of rates $(k_{\rm IC})/(k_{\rm TUN})=0.3$. This predicts that the TKER spectrum for the [D+NHD] channel should include an IC continuum which is 70% of the total signal, which is in qualitative agreement with the conclusions presented in Fig. 5, but that for the $[H+ND_2]$ channel IC would contribute only 10%. For NH₂D the equivalent required ratio of rates is also $(k_{\rm IC})/(k_{\rm TUN})=0.3$. The corresponding predicted proportions of the IC continuum for the [H+NHD] channel is 25%, [and for $(D+NH_2)$, not measured) is 60%]. These various IC contributions to the TKER spectra are also qualitatively correct (see Fig. 4), but tend to underestimate the continuum contribution. However, note from Fig. 4 that there is also a minor continuum contribution to the $[D+ND_2]$ TKER spectrum for ND₃ dissociation (which was assumed to occur by pure tunneling), the neglect of which in the calculations would lead to an under estimation of IC across the whole series. For 0_0^0 band excitation the TKER spectra (Fig. 1) show that internal conversion is of minor importance, even for $[NHD_2 \rightarrow D + NHD]$, and a similar analysis is not possible.

VI. CONCLUSIONS

The calculations presented here should only be taken as qualitative, but they do provide a convincing rationalization of all the observations. We therefore conclude that both



	N =	$=K_a$	N = K	$X_{a} + 1$	N = I	$K_a + 2$	N = 1	$K_a + 3$
K _a	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0		0		14		41		82
1	34	27		54		95		150
2	94	93	127	135		189		257
3	193	200	259	254		323		404
4	347	345	414	413		495		590
5	526	528	610	610	708	705		814
6	750	749	845	844	957	953		1076
7	1009	1006	1119	1115	1242	1238		1374
8	1303	1299	1427	1422	1559	1558		1708
9	1632	1627	1768	1763	1915	1913		2076
10	1991	1988	2144	2138	2307	2301		2478
11	2391	2382	2552	2546	2728	2722		2913
12	2821	2808	2992	2985	3180	3175		3378
13	3277	3265	3463	3455	3660	3658		3875
14	3763	3752	3959	3955	4170	4172		4402
15	4281	4268	4485	4484	4708	4714	4943	4958
16	4822	4813	5040	5042	5272	5286		5541
17	5393	5386	5622	5629	5862	5885		6154
18	5989	5986	6226	6243		6511		6793
19	6607	6614	6860	6883		7164		7459
20		7269		7550		7844		8151
21		7949		8243		8550		8869
22		8656		8962		9282		9614
23		9387		9706		10 037		10 381

TABLE V. Observed and calculated term values/cm⁻¹ for v = 0 levels of NHD(\tilde{X}).

quantum tunneling and internal conversion to high levels of the ground state contribute to the overall dissociation mechanism from excited levels with $v'_2 = 0$ or 1, with a relative importance that varies in a complex way with both the isotopomer and the quantum state excited. The statistical route will add most to the total decay rate for the dissociation of the least symmetrical isotopomers to give the least symmetrical product (NHD), most particularly from excited levels with $v'_2 = 1$ which are the levels with the slowest tunneling rate. The most striking consequence of the effects of symmetry is that for a single excited quantum state of NHD_2 the TKER spectrum for the [H+ND₂] channel has a dominant structured and dynamical character, whereas that for the competitive [D+NHD] channel is largely statistical. Perhaps it was fortunate that we initiated our study of ammonia dissociation dynamics by studying the lowest excited levels of the most symmetrical isotopomers!

We have assumed above that the rates of IC are independent of those for tunneling, consistent with IC directly from the inner well of the excited state. It is possible that part of the outgoing flux on the excited surface could be reflected back onto the ground state surface at the conical intersections, providing an indirect route to IC. Were this to be the dominant IC route the IC rates would be proportional to the tunneling rates, and our model calculations of the branching ratios would be far less successful.

In conclusion, accurate dissociation energies are now available for all the members of the NH_xD_{3-x} series of isotopomers of ammonia. The dissociation dynamics of their first excited states has been shown to involve the mechanisms of quantum tunneling, of IVR through vibrational anharmonicity and/or Coriolis coupling, and through IC, in

proportions which vary over a wide range according to the parent isotopomer and the specific initial excitation. Qualitative models now exist to rationalize all these various data.

Finally, we comment that ammonia shows some aspects of its dissociation dynamics which are typical of the small molecule limit, and others typical of the large molecule limit. The density of states of the ground state at the energy of the first excited state is just sufficient to permit internal conversion from some of the longest-lived quasibound levels. For methane, with one more atom and thus three more internal degrees of freedom, internal conversion has become facile and there is little dynamical character to its dissociation. The ammonia molecule must exhibit more variety to its dissociation dynamics than any other molecule, and is surely *the* text book example of state-selected molecular photodissociation.

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TABLE VI. Potential energy parameters for $NHD(\tilde{X} {}^{2}A'')$.

$f_s = 3.0 \times 10^5 \text{ (cm}^{-1} \text{ Å}^{-1}\text{)}$
$f_b = 33\ 271.2\ (\mathrm{cm}^{-1}\ \mathrm{rad}^{-2})$
$h = 12\ 023.6\ (\mathrm{cm}^{-1})$
$\theta_0 = 76.25 \; (deg)$
$r_0 = 1.0$ (Å)
$c_1 = -167.8 \ (\mathrm{cm}^{-1})$

APPENDIX: TERM VALUES FOR ROTATIONAL LEVELS OF THE GROUND STATE OF NHD ($\tilde{X}^2 A''$)

The experimental rotational term values for NHD (Table V) are derived from the TKER spectrum for $[NH_2D(0_0^0)\rightarrow D+NHD]$ (Fig. 2), with an extrapolated maximum kinetic energy release of 8663 ± 5 cm⁻¹. These were fitted by least squares to model calculations in which, for each $|N, K_a\rangle$ level, the term value was estimated as the minimum value with respect to θ and r of the effective potential function:

$$E_{\rm rot}(N,K_a) = V(\theta,r) + A(\theta,r)(K_a)^2 + \frac{1}{2} [B(\theta,r) + C(\theta,r)] [N(N+1) - (K_a)^2],$$
(A1)

where θ is the external interbond angle, *r* is the NH and ND bondlength, $A(\theta,r)$, $B(\theta,r)$, and $C(\theta,r)$ are "rotational constants" in a principal axis system, and $V(\theta,r)$ is a potential function to be optimized. This model takes explicit account of both centrifugal stretching and centrifugal bending, although it does impose equality of the two bondlengths. The chosen potential function is^{14,25}

$$V(\theta, r) = f_r(r - r_0)^2 + \frac{h f_b(\theta^2 - \theta_0^2)}{[f_b \theta_0^2 + (8h - \theta_0^2)\theta^2]} + \frac{c_1(3\theta^4 - \theta_0^4)\cos(2\pi\theta/5\theta_0)\sin^2(\pi\theta/\theta_0)}{(\theta^4 + \theta_0^4)}.$$
(A2)

The optimum parameters, most of which were taken over from NH_2 ,¹³ are given in Table VI.

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