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

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Photodissociation dynamics of \tilde{A} state ammonia molecules. I. State dependent μ -v correlations in the NH₂(ND₂) products

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

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The H(D) Rydberg atom photofragment translational spectroscopy technique has been applied to a further detailed investigation of the photodissociation dynamics of NH₃ and ND₃ molecules following excitation to the lowest two ($v_2=0$ and 1) vibrational levels of the first excited $(\overline{A}^{-1}A''_{n})$ singlet electronic state. Analysis of the respective total kinetic energy release spectra, recorded at a number of scattering angles Θ [where Θ is the angle between the ϵ vector of the photolysis photon and the time-of-flight (TOF) axis], enables quantification of a striking, quantum state dependent, μ -v correlation in the NH₂(ND₂) products. The spatial distribution of the *total* flux of H(D) atom photofragments is rather isotropic ($\beta_{lab} \sim 0$). However, more careful analysis of the way in which the TOF spectra of the H(D) atom photofragments vary with Θ reveals that each $H+NH_2(D+ND_2)$ product channel has a different "partial" anisotropy parameter, $\beta_{lab}(v_2,N)$, associated with it: The H(D) atom ejected by those molecules that dissociate to yield $NH_2(ND_2)$ fragments with little rotational excitation largely appear in the plane of the excited molecule (i.e., perpendicular to the transition moment and the C₃ axis of the parent, with β tending towards -1). Conversely, the H(D) atoms formed in association with the most highly rotationally excited partner NH₂(ND₂) fragments tend to recoil almost parallel to this C₃ axis (i.e., $\beta \rightarrow \pm 2$). Such behavior is rationalized in the context of the known potential energy surfaces of the A and X states of ammonia using a classical, energy and angular momentum conserving impact parameter model in which we assume that all of the product angular momentum is established at the "point" of the conical intersection in the $H-NH_2(D-ND_2)$ dissociation coordinate. We conclude by reemphasizing the level of care needed in interpreting experimentally measured β parameters in situations where there is averaging over either the initial (parent) or final (product) quantum states. © 1996 American *Institute of Physics.* [S0021-9606(96)01615-0]

I. INTRODUCTION

Photodissociation studies that are fully state resolved, both in the parent molecule and in the resulting products, provide some of the most detailed insight possible into the mechanisms and dynamics of molecular predissociation. Ammonia molecules in their first excited singlet state (the $A^{-1}A_2''$ state) constitute one model system with properties appropriate for this purpose; indeed, given the number and range of recent studies of the dissociation dynamics of \widetilde{A} state ammonia molecules,¹⁻³³ this system must already have acquired the status of being a text book example of a stateselected molecular photodissociation.

Ammonia is a minor constituent of the atmospheres of the outer planets and their satellites, in which photochemical fission produces many important free-radical species which can then participate in further, secondary reactions.³⁴ Photolysis of ammonia initiates the formation of hydrazine. Condensation of this product competes with further photolysis, yielding N₂. This has been advanced as a possible mechanism for the origins of nitrogen in the atmospheres of many of the outer planets and their satellites, specifically Titan.³⁴

The $\tilde{A}^{1}A_{2}'' - \tilde{X}^{1}A_{1}'$ absorption band of ammonia is dominated by a well resolved progression in v_{2}' , the excited

state out of plane (umbrella) bending mode, reflecting the change in minimum energy configuration invoked by optical excitation from the pyramidal ground state to the trigonal planar $\tilde{A} {}^{1}A_{2}''$ state.^{5,9,16} Such a structured absorption cross section allows state selective excitation to specific v'_2 vibrational levels of the \widetilde{A} state. Each 2_0^n vibronic band in the room temperature spectrum will consist of many overlapping rovibronic transitions, each of which is lifetime broadened to an extent that varies sensitively with H(D) isotopic substitution and with the vibrational quantum number(s) of the excited state level.^{1,5,8–13,21,26,32} These dramatic variations in excited state lifetime have been rationalized in terms of vibrational predissociation on the \widetilde{A} state potential energy surface.^{8,10,14,15,24} The \widetilde{A} state of ammonia is quasibound; dissociation from the lowest vibrational levels (i.e., those with $v'_2 \leq 1$) occurs predominantly via H(D) atom tunneling through a barrier in the exit channel leading to the products $H+NH_2(D+ND_2)$. This barrier has been shown to arise as a natural consequence of Rydberg $(3s) \rightarrow$ antibonding valence (σ^*) orbital evolution as one N–H(N–D) bond is extended;² the barrier height is least (and tunnelling consequently most facile) at planar geometries.^{8,14,15,24} \widetilde{A} state ammonia molecules carrying more than one quantum of out of plane bending excitation, or excitation in other vibrational modes, have sufficient internal energy that, if redistributed appropriately,

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

dissociation can occur by passage over (rather than through) this exit channel barrier.

Planarity, or otherwise, affects not just the transmission rate through (or over) the barrier in the N-H (N-D) bond fission channel, but also the asymptotic product correlations. At strictly planar geometries the ground electronic state of ammonia correlates with the excited asymptote associated with H(D) atoms together with $NH_2(ND_2)$ products in their excited $\tilde{A}^2 A_1$ state, whilst the first excited \tilde{A} state of the parent correlates with the ground state products—an H(D) atom plus an NH₂(ND₂) fragment in its ground $\tilde{X}^2 B_1$ state. Away from planarity, both the ground and the excited \overline{A} state of ammonia have the same $({}^{1}A')$ electronic symmetry. Thus the X and \overline{A} state surfaces of the parent can only "cross" at planar geometries and, consequently, there is a conical intersection between these two surfaces, at planar geometries, in the $H-NH_2(D-ND_2)$ exit channel. The parent A state surface is therefore characterized by a deep well in this exit channel, which acts as a funnel, accelerating most of the dissociating trajectories through this narrow region of configuration space onto the X state surface and, hence, to the ground state products. Indeed, for parent excitation at all wavelengths longer than ca. 206 nm (i.e., for A state NH₃ molecules with v'_2 $\leq 3 \ (\leq 4 \text{ for the case of ND}_3)$ ground state fragments are the sole products of this bond fission, excited state product formation being an endoergic process.

The conical intersection has also been shown to have a profound effect on the quantum state population distributions within the resulting NH₂(ND₂) fragments. An early laserinduced fluorescence (LIF) study of the $NH_2(X)$ fragments resulting from ArF laser photolysis of a room temperature NH₃ sample yielded what, at the time, appeared to be an impenetrably complex excitation spectrum, which merely served to indicate that the nascent fragments were born with substantial amounts of internal excitation.³ The first detailed measure of the energy disposal within these products was achieved using the photofragment translational spectroscopy technique pioneered by Welge and co-workers.^{20,23,35} In these early studies,^{20,23} the H atom photoproducts were threshold ionized, at source, using a two color two-photon excitation scheme, resonance enhanced at the one photon energy by the n=2 Rydberg state, and their subsequent times-of-flight monitored. Time-to-energy conversion yielded a spectrum of the total fragment kinetic energy release, the analysis of which showed that the $NH_2(X)$ fragments resulting from dissociation of NH₃ molecules following photoexcitation into each of the first seven bending vibrational levels ($v'_2 = 0-6$) of the \widetilde{A} state were formed with little vibrational excitation, but with substantial amounts of rotational excitation, specifically distributed in the form of *a*-axis rotation. Such markedly nonstatistical energy disposal was shown to be a natural consequence of the conical intersection channelling (and indeed enhancing) any out-of-plane bending motion in the parent NH₃ molecule into *a*-axis rotation in the fragment.²³

More recent studies of the dissociation from the $v'_2 = 0$ and 1 levels of \widetilde{A} state NH₃ employing the alternative neutral (Rydberg) H atom tagging scheme³⁶ yielded significantly higher kinetic energy resolution. This allowed more detailed determination both of the eigenvalues and the relative populations of the individual quantum states of the resulting $\mathrm{NH}_2(\widetilde{X})$ photofragments.²⁵ These data, in turn, permitted the first detailed analysis of the LIF excitation spectrum of the $\mathrm{NH}_2(\widetilde{X})$ fragments resulting from near ultraviolet photolysis of NH_3 .³⁰ The greater detail provided through use of the Rydberg tagging scheme also provided the first clear indications that the distribution of product recoil velocity vectors, **v**, was markedly anisotropic, and that the detailed form of this anisotropy was a function of the particular $\mathrm{H}+\mathrm{NH}_2(\widetilde{X})_{v,N}$ product channel being monitored.

Here we present new high resolution experimental measurements of the kinetic energy distributions of the fragments formed following photoexcitation via both the 0_0^0 and 2_0^1 vibronic bands of the $\widetilde{A} - \widetilde{X}$ transitions of both NH₃ and ND₃. Complementary analyses of the fragments arising from the corresponding photolyses of the much less studied mixed isotopomers of ammonia, NH₂D and NHD₂, are described in the accompanying publication.³⁷ The present high resolution data afford refined eigenvalues for rovibrational levels of ground state ND₂ fragments with rotational quantum number $N \sim K_a$ and for the bond dissociation energies $D_0(H-NH_2)$ and $D_0(D-ND_2)$. More importantly, it also provides the first rigorous study of the previously recognized²⁵ product quantum state dependent correlations between the electric vector of the photolysis laser (ϵ), the transition dipole moment (μ), and the recoil velocity vectors (\mathbf{v}) . This nonclassical stereochemical behavior has been quantified for dissociations following excitation via the origin and the 2_0^1 vibronic bands of the $\widetilde{A} - \widetilde{X}$ transitions of both NH₃ and ND₃, by recording total kinetic energy release spectra for several different values of Θ [the angle between ϵ and the time-of-flight (TOF) axis under otherwise strictly controlled experimental conditions in order to determine effective laboratory frame recoil anisotropy (β) parameters for the dissociation processes leading to each of the individual photofragment quantum states; i.e., what we might view as a series of "partial" β parameters. The observed variations in β with product N are reproduced, qualitatively at least, using a classical, energy and angular momentum conserving, close-coupling impulsive model which approximates NH₃ as a pseudotriatomic $[H-N-(H_2)]$ and assumes that all product angular momentum is generated at the point of the conical intersection in the H–NH₂ dissociation coordinate. Discrepancies between the absolute magnitudes of the experimentally measured laboratory frame anisotropy parameters, β_{lab} , and those predicted by this simple model are rationalised in terms of incomplete alignment of the photoexcited parent molecules.

II. EXPERIMENT

The photofragment translational spectrometer, the photolysis laser, and the laser systems used to "tag" the atomic H(D) fragments have all been described previously^{38–42} and will only be summarized briefly here, along with operational aspects specific to the present studies. A skimmed pulsed supersonic beam of ammonia (or ammonia- d_3)—typically



FIG. 1. H atom TOF spectrum resulting from photolysis of a jet-cooled sample of NH₃ molecules at 46 200 cm⁻¹ with ϵ_{phot} aligned perpendicular to the TOF axis. The inset shows the early time part of this spectrum on a much expanded time base.

seeded as a 1% mixture in argon and held at a total backing pressure of ca. 1 bar-is intercepted at right angles by the output of the three pulsed laser systems used to effect the photolysis and to "tag" the nascent H(D) atom fragments. The recoil kinetic energy distribution of these tagged atoms is determined by recording their collision free TOF to a detector (a Johnston multiplier, type MM1-SG) positioned along the third orthogonal axis with its front face a welldefined distance from the interaction region (825.6 mm for most experiments but, simply because of the way the lab was set up at the time, only 425.6 mm for some photolyses via the NH₃($\widetilde{A} - \widetilde{X}$) 2¹₀ band). The photolysis photons are provided by a Nd-YAG pumped dye laser system (Quanta-Ray GCR-5 plus PDL-3) operating with the dye DCM, the output of which is first frequency doubled (in KDP); the doubled (2ω) and fundamental (ω) outputs are then mixed in BBO to yield the required third harmonic (3ω) radiation. A homebuilt Soleil-Babinet compensator positioned between the two nonlinear crystals served to reorient the respective polarizations of the ω and 2ω beams so as to optimize the sum frequency generation process. The ϵ vector of the resulting 3ω radiation could be rotated (relative to the TOF/detection axis), without any lateral beam displacement, using a Newport RFU 1/2 Fresnel rhomb. The 3ω radiation was then focused (50 cm f.l. lens) so as to spatially overlap, and immediately precede ($\Delta t < 5$ ns), the H(D) atom tagging pulses (fully described previously $^{38-42}$) in the interaction region.

III. RESULTS

A. Bond dissociation energies

Figure 1 shows the TOF spectrum of H atoms resulting from photolysis of a jet-cooled NH₃ sample at 46 200 cm⁻¹, the wave number of the predissociation broadened $R_0(1)$ and $R_1(1)$ transitions and the peak of the *R* branch in the jet-cooled absorption band of the NH₃($\widetilde{A} - \widetilde{X}$) origin transition. The polarization vector of the photolysis laser was aligned perpendicular to the H atom TOF axis. As



FIG. 2. TKER spectrum for the H+NH₂ fragments resulting from photolysis of a jet-cooled sample of NH₃ molecules at 46 200 cm⁻¹ with ϵ_{phot} aligned perpendicular to the TOF axis. Combs above the spectrum indicate the expected kinetic energies of NH₂(\tilde{X}) fragments in their $v_2=0$ and 1 levels with $N=K_a$ and $N=K_a+1$, if we assume a bond dissociation energy $D_0(\text{H}-\text{NH}_2)=37$ 115 cm⁻¹.

previously,^{20,23,25} the structure evident in this TOF spectrum is indicative of the population of quantum states with $N \sim K_a$ in the $NH_2(X)$ partner. Subsequent to the previous studies, however, the eigenvalues of these levels are now known with sufficient precision³⁰ that a spectrum such as this actually serves to provide the most accurate calibration of the distance separating the interaction region and the detector, d, in our photofragment translational spectrometer. Figure 2 shows the total fragment kinetic energy release (TKER) spectrum derived from the TOF spectrum shown in Fig. 1 assuming a flight path d=825.6 mm, the value that affords the minimum standard deviation when least squares fitting the observed kinetic energies of the assigned features in Fig. 2 against their documented eigenvalues. The combs over the spectrum reinforce the earlier findings that the most populated states of the $NH_2(X)$ product are indeed those with v=0 and $N=K_a$, with lesser contributions from states with v = 0 and $N = K_a + 1$ and from the corresponding $N = K_a$ and $K_a + 1$ rotational states built on the $v_2 = 1$ level. Naturally, the availability of such precisely calibrated spectra allows a further refinement of the value for the bond dissociation energy $D_0(H-NH_2)$: Energy conservation requires that

$$E_{\text{int}}(\text{NH}_3) + h\nu = D_0(\text{H}-\text{NH}_2) + E_{\text{kin}}(\text{H}) + E_{\text{kin}}(\text{NH}_2)$$
$$+ E_{\text{int}}(\text{NH}_2). \tag{1}$$

Under conditions of supersonic expansion the chosen photolysis wavelength ($\tilde{\nu}$ = 46 200 cm⁻¹) excites predominantly the $R_0(1)$ and $R_1(1)$ transitions, thus allowing us to estimate a value of ca. 18 cm⁻¹ for $E_{int}(NH_3)$, the average internal energy of the parent molecules undergoing photoexcitation. The input side of the energy balance [Eq. (1)] is thus tightly defined and, given the known NH₂(\tilde{X}) eigenvalues,³⁰ we can derive a very precise value for the total kinetic energy (in the laboratory frame) of the fragments H+NH₂(\tilde{X}), v=0, N=0. We estimate the parent beam velocity (along an axis orthogonal to the TOF axis) at 450±75 m s⁻¹. Applying the laboratory to center-of-mass energy Jacobian results in a 9 cm⁻¹ reduction in the deduced total fragment kinetic ener-



FIG. 3. Calculated absorption profiles (at 15 K) for the 0_0^0 and 2_0^1 bands of the $\widetilde{A}-\widetilde{X}$ transitions of NH₃ [(a) and (b), respectively] and ND₃ [(c) and (d)], with the dominant rovibronic transitions indicated in each case. Spectroscopic parameters for the respective excited states are from Ref. 32.

gies, and a value for $D_0(\text{H}-\text{NH}_2)$: 37 115±20 cm⁻¹ (4.602 ±0.002 eV). This serves to further refine both the value determined in the earlier photofragment translational spectroscopy experiment in which the H atoms were monitored via the ion,²⁰ and the currently recommended literature value.⁴³

Having established a precise measure of the flight path, d, we are in a position to determine bond strengths for the

other isotopomers of ammonia to similar accuracy. Here we concentrate on a comparable analysis yielding $D_0(D-ND_2)$. Discussion of the H-N and D-N bond strengths in the mixed isotopomers NH₂D and NHD₂ is reserved for a companion paper. The lower $(v'_2 = 0 \text{ and } 1)$ vibronic levels of the A state of ND_3 predissociate an order of magnitude more slowly than the corresponding levels in NH₃,^{1,8-10} with the result that the ND₃($\widetilde{A} - \widetilde{X}$) 0_0^0 and 2_0^1 bands show (at least partially) resolved rovibronic structure (Fig. 3) and the initial photoselection of the parent state selection can be that much better defined. Figure 4 shows total kinetic energy release spectra for the $D+ND_2$ fragments (derived using the previously determined value of d) obtained following photoexcitation of jet-cooled samples of ND₃ (1% mixture in Ar) at two different wave numbers—46 708 and 46 724 cm⁻¹, corresponding to the $Q_1(1)$ and $R_0(0)$ transitions in the $ND_3(A - X)$ origin band—and two orthogonal polarizations. These spectra are also dominated by progressions associated with rovibrational levels of the partner fragment with $N \sim K_a$. In the case of $ND_2(\tilde{X})$, however, the energies of the higher $N \sim K_a$ levels are not yet available from high resolution optical spectroscopy. Thus the data shown here, which are substantially better resolved than was apparent in the earlier TOF study of this system²³ (in which the D fragments were monitored via the ion), provides the best measure yet of the eigenvalues of these highly rotationally excited levels of the $ND_2(X)$ fragment.

Our assignments were guided by comparison with esti-



FIG. 4. TKER spectra for the D+ND₂ fragments resulting from photolysis of a jet-cooled sample of ND₃ molecules at 46 708 cm⁻¹ [(a) and (b)] and 46 724 cm⁻¹ [(c) and (d)] with ϵ_{phot} aligned, respectively, parallel [(a) and (c)] and perpendicular [(b) and (d)] to the TOF axis. Combs above each spectrum indicate the expected kinetic energies of ND₂(\tilde{X}) $v_2=0$ fragments with $N=K_a$ and $N=K_a+1$ if we assume a bond dissociation energy D_0 (D–ND₂)=38 010 cm⁻¹.

mated eigenvalues for the $N = K_a$ levels of $ND_2(X)$ calcuusing a "semirigid bender" Renner-Teller lated Hamiltonian^{44,45} with the bending potentials (for the $\tilde{X}^2 B_1$ and $\tilde{A}^2 A_1$ states) optimized by fitting the existing NH₂ data³⁰ with an appropriate change of masses. The calculated term values were then refined by least squares to fit the experimental data. Experimental and predicted eigenvalues for the $N \sim K_a$ rovibrational levels of ND₂(X) are listed in the Appendix. Having established the comb of $N = K_a$ rovibrational energy levels it is then a straightforward matter to determine the total recoil energy of the D atoms formed in association with ND₂(X), v=0, N=0 fragments and thus, after, the necessary small lab to center-of-mass energy correction, to establish a value for $D_0(D-ND_2)=38010\pm 20$ cm^{-1} . As shown in more detail in the following paper, the difference between $D_0(D-ND_2)$ and $D_0(H-NH_2)$ is wholly consistent with the zero-point energy differences between the respective parents (ND₃ and NH₃) and products (ND₂ and NH_2).

B. Product quantum state dependent vector correlations

A previous H atom photofragment translational spectroscopy study²⁵ of the near UV photolysis of NH₃ showed, qualitatively, that the relative intensities of the various peaks appearing in the total kinetic energy release spectra such as those shown in Figs. 2 and 4 were a sensitive function of Θ , the angle between ϵ and the TOF axis. This implies that the fragmentation channels leading to the different H+NH₂ product quantum states have different associated anisotropy parameters, $\beta(v_2, N)$. To further elucidate on the nonclassical angular distribution of photofragments resulting from photolysis via the A state of ammonia, we recorded TOF spectra of the H atoms formed following dissociation of the 0^0 and 2^1 levels of \widetilde{A} state NH₃ (out to $t = 380 \ \mu s$) for a range of Θ values -0° , 15° , 30° , 45° , 60° , 75° , and 90° —while all other experimental conditions were maintained, as near as possible, identical. The angular dependence of the total H atom flux, $Q_{\rm H}(\Theta)$, for excitation via both the 0_0^0 and 2_0^1 bands, is shown in Fig. 5, while the resultant total fragment kinetic energy release spectra at a selection of these angles are displayed in Figs. 6 and 7. (The latter set of spectra were recorded using a shorter flight path, 425.6 mm.)

The corresponding $NH_2(X)$, v_2 , N rovibrational quantum state population distributions were estimated via simulation of the individual spectra.⁴⁶ These simulations proceeded as follows. The eigenvalues for the $NH_2(X)$ partner photofragment are known. Thus we can produce a "spectrum" of δ functions, each of which is then convoluted with a kinetic energy dependent Gaussian line shape function given by $\Delta E/cm^{-1}$ [full width at half maximum (FWHM)] =25+0.0007E, where E is the corresponding total kinetic energy release, in order to reproduce the experimental resolution. The only adjustable parameters then required to model the experimental spectra are the individual peak heights, $W(v_2, N; \Theta)$. At this point we should comment briefly on the rising background at the lowest fragment ki-



FIG. 5. Plots showing the way in which *total* detected H atom flux, $Q_{\rm H}$ (i.e., integrated over all TOF's) resulting from NH₃ photolysis at (a) 46 200 cm⁻¹ (within the $\overline{A} - \overline{X} \ 0_0^0$ band) and (b) 47 069 cm⁻¹ (within the 2¹₀ band) varies as a function of $\Theta,$ the angle between ϵ_{phot} and the TOF axis. For convenience, the vertical scaling has been chosen such that this ratio of H atom fluxes is set to unity at the most favored laboratory scattering angle.

netic energies in both sets of spectra, which appears as a pedestal for $E < 3000 \text{ cm}^{-1}$ in each of the spectra shown in Fig. 6. As discussed more fully in the following paper, we attribute this signal to an alternative predissociation mechanism (internal conversion to high levels of the ground state) which will lead to a much more nearly statistical distribution over all of the energetically available $NH_2(X)$ product quantum states. For the purposes of the present analysis, this underlying continuum signal has been removed by least squares fitting an appropriate function and subtracting its contribution from the experimental result. From the remainder, we can obtain best estimates of the Θ dependence of the relative populations $P(v_2, N; \Theta)$ of the various $NH_2(X)$ product quantum states arising solely from dissociation on the A state surface via the normalization

$$P(v_2, N; \Theta) = \frac{W(v_2, N; \Theta)}{\sum_N \sum_{v_2} W(v_2, N; \Theta)} \frac{Q_{\rm H}(\Theta)}{\sum_{\Theta} Q_{\rm H}(\Theta)}.$$
 (2)

Representative plots for many of the H+NH₂ product channels resulting from photolysis via the 0_0^0 and 2_0^1 bands of the $NH_3(A-X)$ transition are shown in Figs. 8 and 9, respectively. Given the recoil anisotropy relation

$$P(v_2, N; \Theta) = \frac{1}{4\pi} \left[1 + \beta(v_2, N) P_2(\cos \Theta) \right],$$
(3)

where $P_2(\cos \Theta) = \frac{1}{2}(3\cos^2 \Theta - 1)$, we can then estimate a partial anisotropy parameter $\beta(v_2, N)$ for each of these rovi-



FIG. 6. Representative TKER spectra for the H+NH₂ products resulting from fragmentation of a jet-cooled sample of NH₃ molecules following photoexcitation within the $\tilde{A} - \tilde{X} 0_0^0$ band at 46 200 cm⁻¹. These illustrate the way in which the detailed form of this spectrum depends on the relative orientation of ϵ_{phot} and the TOF axis. Combs above each spectrum indicate peaks associated with NH₂(\tilde{X}) fragments in their $v_2 = 0$ and 1 levels with $N = K_a$ and $N = K_a + 1$.

brational product state channels simply by least squares fitting the observed $P(v_2, N; \Theta)$ in terms of Eq. (3) with $\beta(v_2, N)$ as the only unknown. The resultant $\beta(v_2, N)$ are reported in Figs. 10 and 11. These show that, for NH₃ dissociation via the 0^0 level of the \widetilde{A} state, $\beta(v_2, N)$ ranges from ca. -0.7 in the case that the resulting $NH_2(\tilde{X})$ products are formed with little rotational excitation to ca. +1.4 (for the highest $N = K_a$ product states permitted by energy conservation). The observed $\beta(v_2, N)$ parameters for dissociation via the 2^1 level of the A state (Fig. 11) show an even greater sensitivity to the angular momentum and total kinetic energy release; dissociation channels leading to low N products show $\beta \sim -1$ (characteristic of a perpendicular transition; i.e., the detected H atom recoils in the plane perpendicular to the C_3 axis of the parent) whilst the most rotationally excited products arise via a process characterized by a $\beta(v_2, N)$ value of ca. +2 (i.e., the detected H atoms recoil parallel to this axis).

IV. DISCUSSION

This latest study of the near UV photodissociation of jet-cooled ammonia molecules confirms earlier conclusions regarding the very specific channeling of excess energy into *a*-axis rotation of the ground state $NH_2(ND_2)$ fragments, and provides refined eigenvalues for levels of $ND_2(\tilde{X})$ with $N \sim K_a$ and for the respective bond dissociation energies

 $D_0(H-NH_2)$ and $D_0(D-ND_2)$. However, the most notable and original observation, and the one meriting discussion, is the product state dependent recoil anisotropy. A product state dependent anisotropy parameter is not entirely without precedent. For example, the near UV photodissociation of HI yields iodine atoms in both their ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ spin-orbit states; the recoil of the former are consistent with a β parameter of ca. +2 (i.e., recoil parallel to the ϵ vector of the photolysis source) while the latter arise via a perpendicular transition $(\beta \sim -1)$.⁴⁷ This is a somewhat trivial example, reflecting the fact that the near UV photons excite two overlapping *electronic* transitions (the transition moments for which are, respectively, parallel and perpendicular to the internuclear axis) which correlate with the two different spinorbit states of atomic iodine. More pertinent to the present work are recent observations of subtle differences in the effective β parameters for forming various low rotational states of the NO(X) products resulting from near threshold (ca. 396 nm) photolysis of NO₂ (Ref. 48) and for the v = 0 and v = 1NO(X) products resulting from NO_2 photolysis at both 351 and 355 nm,49 although our understanding of the number and nature of the excited electronic states of NO2 involved in these dissociations precludes particularly detailed interpretation of these results.

In contrast, the very striking product N-dependent μ , v correlations observed in the present work are amenable to



FIG. 7. Representative TKER spectra for the H+NH₂ products resulting from fragmentation of a jet-cooled sample of NH₃ molecules following photoexcitation within the $\tilde{A} - \tilde{X} 2_0^1$ band at 47 069 cm⁻¹. These illustrate the way in which the detailed form of this spectrum depends on the relative orientation of ϵ_{phot} and the TOF axis. Combs above each spectrum indicate peaks associated with NH₂(\tilde{X}) fragments in their $v_2 = 0$, 1, and 2 levels with $N = K_a$.

detailed explanation. They are an inevitable consequence of the combined requirements of energy and angular momentum conservation during the passage through, and ultimate fragmentation at, the conical intersection in the $H-NH_2(D-ND_2)$ dissociation coordinate. In what follows we account for the general form of the observed product state dependent μ , v correlations using an extension of the closecoupling impulse model^{41,50} developed to account for the observed rotational state population distribution in the OH(X) products resulting from the Lyman- α photolysis of



FIG. 8. NH₂(\tilde{X} , v_2 , N) quantum state population distributions, P(N), derived from the experimental spectra displayed in Fig. 6 for Θ =(a) 0°, (b) 30°, (c) 60°, and (d) 90° (\blacklozenge , v_2 =0, N= K_a ; \blacksquare , v_2 =0, N= K_a +1; \diamondsuit , v_2 =1, N= K_a ; \bigcirc , v_2 =1, N= K_a +1; the joining lines are included simply to guide the eye).



FIG. 9. NH₂(\tilde{X}, v_2, N) quantum state population distributions, P(N), derived from the experimental spectra displayed in Fig. 7 for Θ =(a) 0°, (b) 30°, (c) 60°, and (d) 90° (\blacklozenge , v_2 =0, N= K_a ; \Box , v_2 =1, N= K_a ; \bigcirc , v_2 =2, N= K_a ; the joining lines are included simply to guide the eye).



FIG. 10. Plots highlighting the variation of the deduced anisotropy parameters, $\beta_{lab}(v_2, N)$ associated with channels leading to $H+NH_2(\tilde{X}, v_2, N \sim K_a)$ produces resulting from photolysis of NH_3 at 46 200 cm⁻¹ (0⁰₀ band) (\blacklozenge , $v_2=0$, $N=K_a$; \blacksquare , $v_2=0$, $N=K_a+1$; \diamondsuit , $v_2=1$, $N=K_a$; \bigcirc , $v_2=1$, $N=K_a+1$; \diamondsuit , $v_2=1$, $N=K_a+1$ products). The solid curves show the result of model calculations employing Eqs. (8)–(10) and assuming a value of +1.1 for the alignment parameter A_0 (see text for further discussion).

H₂O. This purely classical model requires conservation of the total energy and angular momentum, but also involves a number of simplifying assumptions. The ammonia molecule is treated as a pseudotriatomic [(H₂)-N-H]. As discussed earlier, fragmentation to ground state products involves passage through the conical intersection in the H-NH₂ dissociation coordinate. The model assumes that bond rupture is instantaneous at this point of intersection and that it is at this point that the final angular momentum of the products is established; i.e., that this point of conical intersection would represent the 'transition state' for the scattering wave packet. Given our knowledge of the potential energy surfaces for the $A \,\widetilde{}$ and \widetilde{X} states of ammonia and the earlier classical trajectory calculations,²⁴ it is unrealistic to expect the impulsive force to be purely along the dissociating N-H bond-indeed, if this was the case, we should expect the bulk of the available energy to be partitioned into product translation. A more realistic view is that the conical intersection generates a substantial out of plane torque, which carries through as product angular momentum.

We begin by considering the angular momentum of the NH₂ photofragments, \mathbf{j}_{NH_2} . This must equal the vector sum of the angular momentum generated by the recoiling H atom, \mathbf{l}_{H} , and any angular momentum initially present in the parent (\mathbf{J}_{NH_3}). Given that the parent molecules in the present study are internally "cold," this latter contribution will be negligible. Thus,

$$\mathbf{j}_{\mathrm{NH}_2} = -\mathbf{l}_{\mathrm{H}} + \mathbf{J}_{\mathrm{NH}_3} \approx -\mathbf{l}_{\mathrm{H}} \,. \tag{4}$$

The angular momentum associated with the recoiling H atom is the cross product of its recoil momentum and its perpendicular displacement from the center of mass. The magnitude of $\mathbf{l}_{\rm H}$ can be expressed in terms of an impact parameter $b_{\rm N}$,



FIG. 11. Plots highlighting the variation of the anisotropy parameters, $\beta_{\text{lab}}(v_2, N)$ associated with channels leading to $\text{H+NH}_2(\bar{X}, v_2, N \sim K_a)$ products resulting from photolysis of NH₃ at 47 069 cm⁻¹ (2_0^1 band) (\blacklozenge , $v_2=0$, $N=K_a$; \Box , $v_2=1$, $N=K_a$; \bigcirc , $v_2=2$, $N=K_a$ products). The solid curves show the result of model calculations employing Eqs. (8)–(10) and assuming a value of +2.0 for the alignment parameter A_0 (see text for further discussion).

the H atom recoil velocity v_{recoil} , and its reduced mass $\mu_{\text{H-NH}_2}$. Given our assumption that the torque acts at the point of surface intersection, basic geometry implies that

$$b_{\rm N} = R_{\rm CI} \sin \alpha, \tag{5}$$

where $R_{\rm CI}$ is the H–NH₂ distance at the conical intersection and α is the final angle of recoil measured relative to the D_{3h} plane of the excited state molecule as shown in Fig. 12. Thus we can write

$$|\mathbf{j}_{\mathrm{NH}_2}| \approx |\mathbf{l}_{\mathrm{H}}| = b_N \mu_{\mathrm{H-NH}_2} v_{\mathrm{recoil}} = R_{\mathrm{CI}} \sin \alpha \mu_{\mathrm{H-NH}_2} v_{\mathrm{recoil}}.$$
(6)

Simple energy conservation [Eq. (1)] allows us to write

$$h\nu - D_0(H-NH_2) = \frac{1}{2}\mu_{H-NH_2}v_{\text{recoil}}^2 + E_{\text{int}}(NH_2),$$
 (7)



FIG. 12. Illustration of the impact parameter model used to account for the experimentally observed correlation between the recoil velocity, **v**, and the rotational angular momentum, **j**, of the N+NH₂ products resulting from near UV photolysis of jet-cooled NH₃ molecules. The model treats NH₃ as a pseudotriatomic molecule [(H₂)–N–H] and assumes that all product angular momentum is established at the point of the conical intersection between the X^{-} and \tilde{A} state potential energy surfaces of the dissociating parent molecule (see text for further details).

where $\frac{1}{2} \mu_{\text{H-NH}_2} v_{\text{recoil}}^2$ is the total kinetic energy of the recoiling fragments. Rearranging Eqs. (6) and (7) so as to eliminate v_{recoil} , and reexpressing $|\mathbf{j}_{\text{NH}_2}|$ in terms of $N \ (\equiv K_a \text{ in this model})$, we obtain

$$\sin \alpha = \frac{[N(N+1)\hbar]^{1/2}}{R_{\rm CI} \{2\mu_{\rm H-NH_2} [h\nu - D_0(\rm H-NH_2) - E_{\rm int}(\rm NH_2)]\}^{1/2}}.$$
(8)

Thus we have established a simple relationship between the out-of-plane recoil angle α (in the body-fixed frame of the molecule) and the final rotational angular momentum of the products. The corresponding anisotropy parameter, β (in the body fixed frame with a parallel transition dipole) associated with each $|v_2, N\rangle$ product channel is therefore

$$\beta(v_2, N) = 2P_2[\cos(\pi/2 - \alpha)] = \frac{3N(N+1)\hbar^2}{2\mu R_{Cl}^2 [E_{avail} - E_{int}(NH_2)]} - 1.$$
(9)

Note from Eqs. (8) and (9) that, for a given available energy and $R_{\rm CI}$, there is an upper limiting value of N for which these equations are applicable. This occurs when a product channel is closed at finite $R_{\rm CI}$ by a high centrifugal barrier.

Quantifying $R_{\rm CI}$ is not trivial, since the "point" of conical intersection is in fact a surface involving four of the six dimensions needed to represent the complete potential energy surface of NH₃. For the purpose of this calculation we assume a value of $R_{\rm CI}$ =0.196 nm derived from inspection of Figs. 2 and 4 of Ref. 15, but a 10% variation in this value would have little effect on the overall conclusions that follow. The calculated values so obtained for the NH₂ $|v_2=0,$ $N=K_{a}$ products arising from photolysis via the 2¹ level of NH₃(A) at 47 069 cm⁻¹ are shown by the smooth curve superimposed upon the experimental data in Fig. 11(a). Clearly, the general form of the calculated $\beta(v_2, N)$ values reproduces the trends of the measured $\beta_{\rm lab}(v_2, N)$ values for this and the other sets of populated states almost quantitatively, being negative for the low N product states, approaching zero at intermediate N and then becoming strongly positive for the highest $N \sim K_a$ product states. Thus we conclude that low angular momentum states are created when the H atom is ejected perpendicular to the C₃ top axis of NH₃, but that the combination of energy and angular momentum conservation requires that the recoil velocity vectors of those H atoms that are formed in association with the highest $N = K_a$ product states must be aligned almost parallel to this top axis. It should be noted that for $K_a = 21$ and this total energy Eq. (8) is inapplicable with $R_{CI}=0.196$ nm. Thus this product channel must become populated with an impact parameter b_N larger than the chosen value of R_{CI} , thereby indicating a limitation of the assumption of simple rectilinear trajectories through a single action point.

Finally we need to address the fact that our measurements are made in the laboratory, not the body fixed, frame and, although the trends in the experimentally derived $\beta_{\text{lab}}(v_2, N)$ values observed for dissociation via the 0^0 and 2^1 levels of \overline{A} state NH₃ are very similar, their absolute magnitudes differ by some 30% (see Figs. 10 and 11). This reflects a combination of two factors, neglected in our discussion thus far: parent alignment, and the finite time scale of the fragmentation process.²⁵ Concentrating on the former first; the respective photoexcitation processes produce excited state populations with differing degrees of alignment, which should be reflected in the measured lab frame anisotropy parameters according to

$$\beta_{\rm lab} = A_0(J', K') \langle P_2(\cos \alpha) \rangle. \tag{10}$$

As Fig. 3 shows, the jet-cooled absorption associated with the NH₃($\widetilde{A} - \widetilde{X}$) 2_0^1 band is dominated by the $R_0(0)$ transition, for which the excited state alignment parameter A_0 will take the limiting value +2.0, and our impact parameter model thus predicts $\beta_{lab}(v_2, N)$ values ranging from -1 to +2 [Eq. (10)]. However, the corresponding transition is symmetry forbidden in the $NH_3(A-X)$ origin band and, under the prevailing experimental conditions, our photoexcitation will involve (predominantly) the predissociation broadened $R_0(1)$ and $R_1(1)$ lines, having relative intensities ca. 2:1 at 15 K. The spatial alignment parameters associated with these two excitations are +1.0 and +0.5, respectively, with the weighted mean ca. +0.83. This would imply that the resulting excited state molecules would precess such that the plane containing the nuclei makes an average angle of ca. 62° with the transition dipole μ . In practice, the experimental $\beta_{lab}(v_2, N)$ values measured following excitation via the $NH_3(A-X)$ origin band are less degraded than would be predicted by including this value of A_0 in Eq. (10). This is understandable given the finite time scale of the dissociation process. The parent absorption spectrum shows predissociation broadened linewidths of ca. 38 cm⁻¹ (FWHM),^{10,12,26} implying an excited state lifetime with respect to fragmentation (ca. 1.4×10^{-13} s) that is short in comparison with one complete rotational period for an NH₃ molecule with J=1. Thus it should come as little surprise that the recoil anisotropies we observe following excitation via the $NH_3(A - X)$ origin band are (i) smaller than those we measure following

TABLE I. Observed and calculated term values (in cm⁻¹) for levels of the $X^{-2}B_1$ state of ND₂.

	v ₂ =0					$v_2 = 1$
		$N = K_a$		$N = K_a + 1$	$N = K_a + 2$	$N = K_a$
K _a	Obs.	Calc.(a)	Calc.(b)	Calc.(b)	Calc.(b)	Calc.(a)
0		0	0	11	32	1100
1		19	19	40	72	1120
2	64	64	64	96	139	1168
3	136	136	136	179	232	1244
4	234	234	234	287	351	1348
5	356	358	357	421	496	1479
6	506	506	506	581	666	1637
7	677	680	679	765	861	1820
8	874	877	876	973	1080	2027
9	1096	1097	1096	1204	1322	2258
10	1340	1339	1338	1457	1587	2512
11	1604	1603	1602	1732	1874	2788
12	1886	1888	1886	2028	2181	3085
13	2192	2193	2191	2345	2509	3402
14	2516	2517	2515	2680	2856	3739
15	2857	2860	2857	3034	3222	4093
16	3221	3221	3218	3406	3606	4466
17	3600	3600	3595	3796	4008	4855
18	3996	3995	3989	4202	4426	5261
19	4408	4406	4399	4624	4861	5682
20	4843	4832	4824	5062	5311	6119
21	5270	5273	5264	5514	5776	6569
22	5723	5728	5718	5981	6256	7034
23	6200	6197	6186	6462	6749	7511
24	6686	6679	6668	6956	7256	8001
25	7181	7174	7162	7464	7777	8503
26	7693	7681	7668	7983	8309	9017
27		8200	8186	8515	8854	9542
28		8730	8716	9058	9411	10 077
29		9270	9257	9613	9980	10 623
30		9821	9809	10 178	10 559	11 178

excitation of the fully aligned NH₃(\tilde{A} ,2¹) molecules but (ii) not as degraded as might be predicted in the limit that the excited state alignment was allowed to develop over several rotational periods. The solid curves in Fig. 10 are fits to the experimental data derived using Eqs. (8)–(10) and an ''effective'' A_0 value of +1.1.

Our measurements involving ND₃ are less extensive in the sense that we only made measurements with two orthogonal photolysis laser polarisations, but they do involve a very high degree of initial state selection. The angular dependence of the data shown in Fig. 4 are entirely consistent with all of the foregoing discussion. Excitation at 46 724 cm⁻¹ invokes the $R_0(0)$ transition of the ND₃ $(\tilde{A} - \tilde{X})$ origin band; the resulting excited state molecules having J'=1 and K'=0 will be fully aligned ($A_0 = +2.0$). Once again, notwithstanding the longer excited state lifetime with respect to dissociation (ca. 1.3×10^{-12} s), we observe a marked *N*-dependent μ , v correlation in the products as predicted in the original theoretical treatment of such correlations.⁵¹ This correlation is much less evident in the data taken at 46 708 cm^{-1} [Figs. 4(a) and (b)]. In this latter case we are exciting, predominantly, the $Q_1(1)$ transition, leading to population of the J'=1, K'=1 level and the reduced correlation is entirely attributable to the much poorer alignment of the excited state molecules ($A_0 = +0.5$); note that these two J' = 1 levels differ in total energy by just 2.6 cm⁻¹.

V. CONCLUSIONS

H (Rydberg) atom photofragment translational spectroscopy has been applied to a further detailed investigation of the photodissociation dynamics of NH₃ and ND₃ molecules following excitation to the lowest two ($v_2=0$ and 1) vibrational levels of the first excited ($\tilde{A}^{-1}A_2''$) singlet electronic state. Analysis of the respective total kinetic energy release spectra confirm earlier conclusions that, in each case, the NH₂(ND₂) fragments are formed with little vibrational excitation but with high levels of rotational excitation, specifically distributed in the form of rotation about the *a*-inertial axis. The present work provides refined values for the respective bond dissociation energies: D_0 (H–NH₂) =37 115±20 cm⁻¹, D_0 (D–ND₂)=38 010±20 cm⁻¹.

The most striking aspect of the present work, however, is the particularly clear demonstration of, and quantification of, the way in which the measured recoil anisotropy parameter depends on the particular quantum state in which the $NH_2(ND_2)$ product is formed. The spatial distribution of the *total* flux of H(D) atom photofragments is fairly isotropic $(\beta_{lab} \sim 0)$. However, more careful analysis of the way in which the TOF spectrum of the H(D) atom photofragment varies with Θ , the angle between ϵ and the TOF axis, reveals that each $H+NH_2(D+ND_2)$ product channel in fact has a different effective anisotropy parameter, β_{lab} , associated with it. The H(D) atom ejected by those molecules that dissociate to yield $NH_2(ND_2)$ fragments with little rotational excitation appear largely in the plane of the excited molecule (i.e., perpendicular to the transition moment and the C₃ axis of the parent, with β tending towards -1). Conversely, the H(D) atoms formed in association with the most highly rotationally excited partner NH₂(ND₂) fragments tend to recoil almost parallel to this C₃ axis (i.e., $\beta \rightarrow +2$). Such behavior has been rationalized in the context of the known potential energy surfaces of the \widetilde{A} and \widetilde{X} states of ammonia using a classical, energy and angular momentum conserving impact parameter model in which we assume that all of the product angular momentum is established at the "point" of the conical intersection in the $H-NH_2(D-ND_2)$ dissociation coordinate. Other simple systems where we can anticipate that such product state dependent μ , v correlations might be observable are (obviously) the heavier Group V hydrides, but also

TABLE II. Potential energy parameters for ND₂(\tilde{X}^2B_1) used for calculations (b) of Table I.

$f_s = 3.0 \times 10^5 (\text{cm}^{-1} \text{\AA}^{-1})$	
$f_b = 33 \ 271.2 \ (\text{cm}^{-1} \ \text{rad}^{-2})$ $h = 12 \ 023.6 \ (\text{cm}^{-1})$	
$\theta_0 = 76.0$ (deg)	
$r_0 = 1.0 \text{ (A)}$ $c_0 = -167.8 \text{ (cm}^{-1}\text{)}$	
$c_1 = 107.0$ (cm)	

any bent triatomic molecules where photodissociation occurs following a linear \leftarrow bent transition for which the transition dipole moment lies in the molecular plane.

This study serves as a timely reminder of the need for caution when interpreting β parameters determined from non fully quantum state resolved experimental measurements of the photofragments arising even from as small and simple a polyatomic molecule as ammonia. Traditionally, it has long been recognized that measured β parameters intermediate between the limiting values of +2.0 and -1.0 (corresponding to the case of prompt dissociation following photoexcitation via a transition whose dipole moment lies, respectively, parallel and perpendicular to the molecular plane) can reflect (i) the presence of overlapping transitions in the parent absorption spectrum and/or (ii) a reduction in anisotropy due to parent rotation during the lifetime of the photoexcited molecule. The present study highlights more of the subtleties that may be 'buried' in such measurements. For example, dynamical factors may dictate (as here) that each product channel has its own, well defined β parameter: as we show, a simple measurement of the angular dependence of the *total* flux of either product returns an average (and dynamically meaningless) β value. By way of further complication we demonstrate that, in the case of predissociative systems at least, one should give detailed consideration to the way in which parent alignment will affect the actual magnitude of any measured β parameter, even when measured with full quantum state resolution of the products. From the aforementioned discussion it should be obvious that we would expect that simply changing the photolysis energy by a few cm^{-1} would result in population of a different "mix" of excited state levels, with different alignments, leading to products with somewhat different recoil anisotropies and thus $\beta(v_2, N)$ values which, whilst showing similar trends to those displayed in Figs. 10 and 11, can be expected to differ in their absolute magnitudes.

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APPENDIX: TERM VALUES FOR ROTATIONAL LEVELS OF THE GROUND STATE OF ND₂($\tilde{X}^{2}B_{1}$)

The assignments of the TKER spectra were based on calculated eigenvalues using the "semirigid bender" Renner–Teller Hamiltonian,^{44,45} with the bending potentials (for the \tilde{X}^2B_1 and \tilde{A}^2A_1 states) optimized by fitting the existing NH₂ data,³⁰ and with an appropriate change of masses for ND₂. The experimental rotational term values for $v_2=0$ and $N=K_a$ (Table I) were then derived from the TKER spectrum for [ND₃(0⁰₀) \rightarrow D+ND₂] (Fig. 4), with an extrapolated dissociation energy of D_0^0 (D–ND₂)=38 010 cm⁻¹.

These Renner–Teller calculations slightly underestimate the experimental term values, indicating a small mass dependence to the variation with K_a of the contribution from the zero-point energy of the neglected stretching vibrations. The term values denoted as calc.(a) in Table I are derived from these Renner–Teller calculations by applying a uniform scaling increase of 0.9%.

The experimental term values for $v_2=0$ and $N=K_a$ were also fitted by least squares to a more empirical model in which, for each level $|N, K_a\rangle$, the term value was estimated as the minimum value with respect to θ and r of a single 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 inter bond angle, *r* is the NH bond length, $A(\theta,r)$, $B(\theta,r)$, and $C(\theta,r)$ are "rotational constants" in the 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. The chosen potential function was^{30,44}

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

The optimum parameters, most of which were taken over from NH₂,³⁰ are given in Table II. This model was then used to calculate term values for $v_2=0$ and $N>K_a$. Term values calculated by this method are denoted as calc.(b).

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