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Internal Energy Distributions of NH($A^3\Pi$). An Application of Phase Space Theory to the Electron-impact Dissociation

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Internal energy distributions of NH(A) produced by electron impact on NH_3, HN_3, and HNCO are compared with those predicted by use of the phase space theory based on the method of Light and Pechukas. The values predicted under conservation of energy and total angular momentum are found to be inconsistent with the experimental results. The observed values are well simulated *via* the introduction of a nonstatistical bias by representing the selective coupling between the reaction coordinate and the rotational modes of the products. The dynamics for formation of NH(A) is discussed.

The decomposition of polyatomic molecules is a typical example of unimolecular reactions. Unimolecular processes only proceed at an appreciable rate when the reacting molecule posseses an internal energy greater than a certain threshold value corresponding to the activation energy. These active molecules arise in the process of chemical reaction as a result of inelastic molecular collisions, or on electron, or photon, impact. The basic idea of the statistical theory of unimolecular reactions[1] is that an active molecule is considered as a closed system whose states are distributed with equal probability over hypersurfaces of constant total energy.

The transition state theory[2] of chemical reactions identifies the transition complex having activation energy along the reaction coordinate. In the reactions such as bond dissociations, however, there is little or no potential-energy barrier along the reaction coordinates. Light and Pechukas[3] treated atom-molecule reactions which proceed without activation energy under the requirement that the reaction complex can dissociate over the orbital angular momentum barrier in the final state. Their method was successfully applied to the photodissociation $NH_3 \rightarrow NH(c^1\Pi)+H_2$.[4] Mies[5] pointed out that their space theory is a special microcanonical version of the transition state theory for the "loose complex," where the activated complex is the rotational barrier in the asymptotic channel. Horie and Kasuga[6] proposed another statistical model including the law of angular momentum conservation and discussed the decomposition $H_2O \rightarrow H+OH(A^2\Sigma^+)$ through electron or photon impact.

We previously reported formation and internal energy distributions of NH($A^3\Pi$) by electron impact on NH_3,[7] HN_3,[8] and HNCO.[9] The basic idea of Light and Pechukas[3] can be applied to these electron-impact dissociations. In the present paper, the observed distributions of NH(A) from NH_3, HN_3, and HNCO are compared with those predicted by a statistical calculation based on the method of Light and Pechukas.[3] In order to give an account of the observed values, we have introduced a nonstatistical bias by representing the selective coupling between the reaction coordinate and the rotational mode of the products. On comparison between the observed distributions and the predicted by the statistical calculations, the dynamics for formation of NH(A) is discussed.

Method of Calculation

Outline of Calculation. The main requirements imposed on the system[1] are that the reaction proceeds *via* an intermediate complex with a long lifetime and that the coupling between different degrees of freedom must ensure a sufficiently intensive energy exchange between them. This statistical theory assumes that the size of the phase volume accesible to the active and activated molecules is limited only by the condition that the energy is constant. Furthermore, conservation of the total angular momentum of the system imposes an additional restriction on the size of the phase volume of the active and activated molecules. This restriction is especially important for "loose" activated molecules. Moreover, the conservation of angular momentum is important when the active molecule arises as a result of excitation by electron impact. This is connected with the fact that, due to electron impact, a large amount of electronic-vibrational excitation energy is usually transferred to the molecule, but the rotational angular momentum of the molecule is very little changed.

To evaluate the energy distribution, we introduce the available energy (E_{av}) defined by the difference between the vertical and the adiabatic energy required for decomposition. The probability of decomposition of the parent molecule to a given state is the same to all the states to be accessible under conservation of energy and total angular momentum. Thus, for this system, the validity of the microcanonical distribution is assumed. Accordingly, after decomposition, E_{av} is allowed to be distributed among all the degrees of freedom in the products. The initial angular momentum $\boldsymbol{J}$ (momentums are written throughout in units of $\hbar$) possessed by the parent molecule as molecular rotation must be equal to the sum of those of the molecular rotations of the fragments and the orbital angular momentum between them.

Theoretical Energy Distributions of the NH(A) Product.

We treat here a direct dissociation into final fragments such as Reactions 1 and 2, and do not consider an indirect process such as Reaction 3, where one of the products are quasibound in an intermediate state.

$$NH_3 \longrightarrow NH(A)+H_2(X), \tag{1}$$

$$NH_3 \longrightarrow NH(A)+H(1s)+H(1s), \tag{2}$$

$$NH_3 \longrightarrow NH_2{}^*+H(1s), \tag{3a}$$

$$NH_2{}^* \longrightarrow NH(A)+H(1s), \tag{3b}$$

$$HN_3 \longrightarrow NH(A)+N_2(X), \tag{4}$$

$$HNCO \longrightarrow NH(A)+CO(X). \tag{5}$$

The calculation of the internal energy distributions was carried out on the basis of the following methods: Method 1 is a simple statistical calculation under the requirement of conservation of energy. Method 2 is the statistical calculation based on the method of Light and Pechukas.[3] In Method 3, a nonstatistical bias is introduced into the population distribution.

In the case of a reaction such as M→NH+B, where B is a diatomic molecule, $\boldsymbol{J}_N$, $\boldsymbol{J}_B$, $\boldsymbol{J}$, $\boldsymbol{l}$, $\boldsymbol{k}$, their space-fixed z components, v_N, and v_B can be used to specify the quantum states of all the products. The v_N and v_B are the vibrational quantum numbers of NH and B, respectively. The $\boldsymbol{J}_N$ and $\boldsymbol{J}_B$ are the rotational angular momenta of NH and B, respectively, $\boldsymbol{l}$ is the orbital angular momentum among the fragments, $\boldsymbol{k}$ is an intermediate angular momentum associated with a vector sum $\boldsymbol{J}_N+\boldsymbol{J}_B$, and $\boldsymbol{J}$ corresponds to the total angular momentum $\boldsymbol{J}=\boldsymbol{k}+\boldsymbol{l}$. The angular momenta are restricted by energy conservation and by the triangle inequalities:[10] namely, the corresponding quantum numbers k and J can have the values $|J_N-J_B|\leq k\leq J_N+J_B$ and $|k-l|\leq J\leq k+l$.

On the assumption of a Boltzmann temperature of 298 K for the ground state of parent molecules, the distribution of J, $P(J)$, was evaluated by use of the rotational constants.[11] The total number of the J state among various product states with E_{av} is given by

$$N(J,E_{av})=\sum_{v_N}\sum_{v_B}\sum_{J_N}\sum_{J_B}\sum_{l=0}^{l_{max}} 1, \tag{6}$$

under conservation of total energy that $E_{av}=E_{tr}+E_{rot}+E_{vib}$, where E_{tr} denotes the translational energy, and E_{rot} and E_{vib} are the rotational and the vibrational energies of all the fragments,[12] respectively. Light and Pechukas[3] derived the quantum number of the maximum orbital angular momentum, l_{max}, from the interaction potential between the products. However, no information is found about the interaction potential among the fragments from parent molecules. In this study, the interaction constant (spherically averaged sum of dipole-induced dipole and dispersion contributions) denoted by C are estimated on the basis of the method of Hirschfelder *et al.*[13] by use of data on the polarizabilities, dipole moments, ionization potentials for H[14] and diatomic fragments.[12,13] Dipole moment and polarizabiliy of NH(A) are assumed to be 3.34×10^{-30} Cm (1 D) and 1×10^{-30} m^3, respectively. The interaction constants thus obtained are listed in Table 1. In preliminary analysis, the internal energy distributions evaluated are found to be rather insensitive to l_{max}.

The probability of dissociation into each accessible final state having J is $P(J)/N(J,E_{av})$. Thus, the rotational distribution in the v_N level of NH(A) can be reperesented with collection of all the states having J_N and v_N as follows:

$$P(J_N,v_N,E_{av})=\sum_{v_B}\sum_{J_B}\sum_{l}\sum_{J}P(J)/N(J,E_{av}), \tag{7}$$

under the conservation of energy and the restriction based on the two triangle inequalities on angular momenta. In Reaction 2, we must exclude summation over v_B and J_B from Eqs. 6 and 7. Equation 7 is summed to give the vibrational distribution of NH(A),

$$P(v_N,E_{av})=\sum_{J_N}P(J_N,v_N,E_{av}). \tag{8}$$

In calculation of the rotational distribution of NH(A) by Method 1, Eq. 7 is replaced by

$$P(J_N,v_N,E_{av})=\sum_{v_B}\sum_{J_B} 1, \tag{9}$$

where the sum includes, of course, the accessible states under conservation of energy.

In electron-impact dissociation at energies over the onset for formation of NH(A), an available energy (E_{av}) converting into the translational and internal energies of products cannot be given very clearly because collisions with electrons are essentially an energy-loss process. Thus, E_{av} was treated as an adjustable parameter.

Following a series of diagnostic calculation for Reactions 1, 2, 4, and 5, a nonstatistical bias is introduced into the rotational distribution (Method 3) with the view of agreement with the observed values: namely, Eq. 7 is multiplied by a factor of $\exp(-\beta|E_{av}-E_{rot}|)$, where β is a parameter representing the strength of coupling between the reaction coordinate and the rotation of the fragments. This factor realizes the resonance feature in energy transfer of the available energy into the rotation of the fragments. Thus, in Method 3, the validity of the microcanonical distribution no longer holds good. The parameter β represents insufficientness in energy exchange among various degrees of freedom at the energy partitioning process.[15] When β decreases to zero, Method 3 apparently results in Method 2.

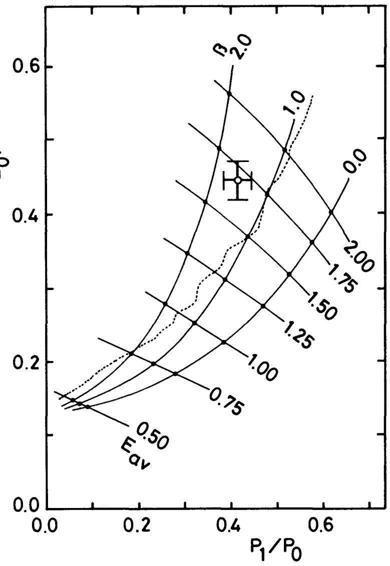

Fig. 1. Rotational energy (E_0) *versus* vibrational population ratio (P_1/P_0) predicted for Reaction 1: the open circle with error bars shows the observed values at electron energy of 17 eV. The dotted line shows the results by Method 1. The solid line with $\beta=0$ shows those by Method 2 and the others with $\beta=1.0$ and 2.0 show those by Method 3.

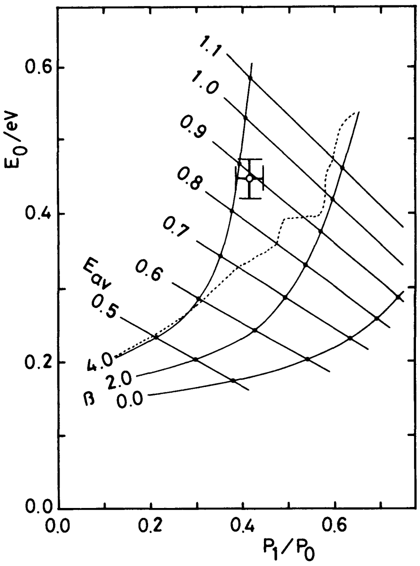

Fig. 2. The same as Fig. 1 but for Reaction 2.

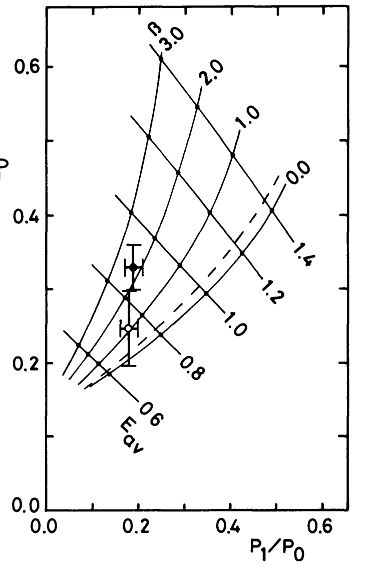

Fig. 3. The same as Fig. 1 but for Reaction 4. The open and the closed circles with error bars show the results at electron energies of 7 and 10 eV, respectively.

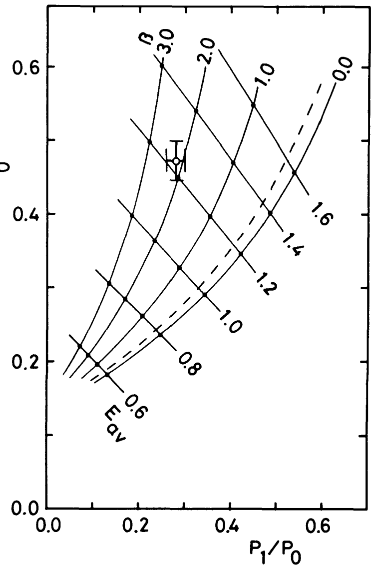

Fig. 4. The same as Fig. 1 but for Reaction 5.

Results and Discussion

Vibrational Population Ratio versus *Rotational Energy of NH(A).* In the analysis of the emission intensities of the NH(A-X) spectrum, we used the relative vibrational population ($P_v/P_{v=0}$) and the rotational temperature (T_v) of the $v=0$ and 1 levels of the NH(A) state. Although the rotational distribution evaluated by use of the statistical methods can be approximated by a Boltzmann temperature, the population decreases more rapidly with increasing J_N and disappears suddenly. Henthforce, the observed rotational distributions were compared with those predicted in the form of E_v being the rotational energy concerning with the v level.

In Figs. 1—4, E_0 is plotted *versus* P_1/P_0 comparing the observed values with the predicted by three methods. The observed results from NH_3 and HN_3 are nearly consistent with the predicted by Method 1 for Reactions 1 and 4, respectively, but are inconsistent with those by Method 2. On the contrary, the results predicted for Reactions 2 and 5 by both Methods 1 and 2 cannot explain the observed values from NH_3 and HNCO, respectively. These imply that the agreement between the observed and the predicted for

TABLE 1. THE P_1/P_0 AND E_0 OBSERVED AND PREDICTED WITH THE BEST FIT E_{av} AND β

Molecules Reactions	Methods	P_1 / P_0	E_0 / eV	E_{av}[a] eV	β[a] eV^{-1}	C 10^{-78} J m^6
NH_3	Obsd[b]	0.415±0.02	0.447±0.03			
1	1	0.460	0.403	1.40	—	
1	3	0.415	0.447	1.685	1.515	1.83
2	1	0.490	0.392	0.75	—	
2	3	0.414	0.446	0.893	3.686	1.23[c]
HN_3	Obsd[d]	0.18±0.01	0.245±0.05			
4	1	0.214	0.233	0.8	—	
4	3	0.182	0.248	0.75	1.01	2.74
HNCO	Obsd	0.28±0.02	0.48±0.04			
5	1	0.44	0.387	1.4	—	
5	3	0.280	0.471	1.23	2.06	2.92

a) The best fit values used for simulation. b) Observed at electron energy of 17 eV. c) Sum of one H-H and two NH-H attractive contributions. d) Observed at electron energy of 7 eV.

Reactions 1 and 4 by Method 1 is specious because Method 2 is more accurate than Method 1. Accordingly, in order to explain the observed results, we have introduced a nonstatistical bias and have adjusted not only E_{av} but the coupling parameter β. Table 1 lists the predicted E_0 and P_1/P_0 by use of best fit E_{av} and β comparing with the observed.

Recently, Kajimoto[15] has treated the rotational distributions of NH($c^1\Pi$) through photolysis of NH_3 by use of a nonstatistical bias representing the coupling between the bending motion of NH_3 precursor and the rotation of NH(c). On the assumption of vibrational energy of 21 kJ/mol (0.22 eV) for bending motion of NH_3, the observed distributions has been well simulated by use of β=0.024 mol/kJ (2.3 eV^{-1}). On the contrary, the best-fit E_{av} and β for formation of NH(A) through electron impact on NH_3, HN_3, and HNCO are 0.8—1.7 eV and 1.0—3.7 eV^{-1}, respectively. This implies that many vibrational motions of precursor are strongly coupled with the rotation of NH(A).

Formation of NH(A) from NH_3. In electron-impact dissociation of NH_3, NH(A) is produced *via* two different channels.[7] One corresponds to Reaction 1 *via* a triplet precursor with the onset energy of 8.0 eV and the other corresponds to Reaction 2 with the onset energy of 12.3 eV. Reactions 1 and 2 similarly contribute to the formation of NH(A) at the lowest impact energy of 17 eV, to which the population analysis could be applied, while Reaction 2 is main contributors of the formation of NH(A) above 17 eV. The rotational distributions of the v=0 and 1 levels of NH(A) are found to vary only moderately from 17 up to 92 eV. This indicates that the rotational distribution of NH(A) produced *via* Reaction 1 is nearly equal to those *via* Reaction 2.

The observed values are shown in Fig. 5 comparing with the results predicted for Reactions 1 and 2. The distributions predicted for Reaction 1 is in fairly good agreement with the observed, while those for Reaction 2 is inconsistent with the observed. The results for Reaction 1 by Method 3, however, rather overestimate the distributions of the v=1 level above J_N=15. This is due to the application of single coupling constant β to the distributions of both the v=0 and 1 levels. The difference between the observed distributions and the predicted for Reaction 2 seems to originate in the application of the method of Light and Pechukas.[3]

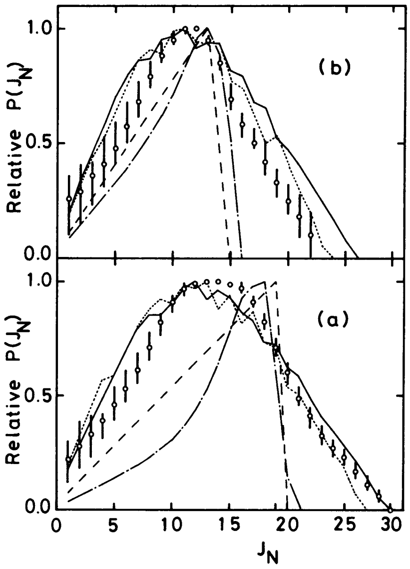

Fig. 5. The relative rotational distributions of NH(A) from NH_3 for (a) the v=0 level and (b) the v=1 level: ------, Method 1 for Reaction 1; ——, Method 3 for Reaction 1; — — —, Method 1 for Reaction 2; —·—·—, Method 3 for Reaction 3. The open circles with error bars show the observed values.

In unimolecular reactions into an atom(s)+diatomic product such as Reaction 2, the predicted distribution is extremely nonthermal and strongly depends on E_{av}. In case of electron-impact excitation, the electron energy for impinging electron is not so monoenergetic, contrary to photon excitation. On the basis of the Franck-Condon principle, the distribution of E_{av} may be determined by reflecting the position probability function associated with the normal vibrations of the ground state of parent molecule onto the potential energy surface of the precursor state. Accordingly, E_{av} is expected to have a rather broad distribution. In such a case, it is necessary to take the weighted mean of the population distributions obtained for a wide range of values of E_{av}. On the assumption of a Gaussian distribution for E_{av}, Horie and Kasuga[6] reproduced the rotational distribution of OH(A) produced by electron impact on H_2O. When both the ground and the precursor states of NH_3 are well informed, we expect to give an account of the observed rotational distribution of NH(A) for Reaction 2 by Method 3 using a suitable distribution of E_{av}. On the contrary, in unimolecular reactions into two diatomic products such as Reactions 1, 4, and 5, the predicted distribution is nearly thermal and only moderately depends on E_{av}. In this case, even if we do not consider the distribution of E_{av}, we can reproduce the observed distribution by use of the best fit E_{av} and β. The value of E_{av} thus obtained means rather an averaged value. Incidentally, for Reaction 3b, calculation of the internal energy distributions of NH(A) by Method 2 by use of a variety of Boltzmann temperatures for NH_2* failed in agreement with the observed.

Runau *et al.*[16] reported in their *ab initio* study that the SCF potential curve calculated for Reaction 1 correlates with the $^3A_2''$ state (point group D_{3h}), which corresponds to excitation out of the $3a_1$ (C_{3v}) MO into the $4a_1$ (Rydberg 3s+H 1s) orbital. This $^3A_2''$ precursor (the lowest triplet state) belongs to the Rydberg state having a planar geometry since one of the lone pair electrons is mainly excited into the atomic orbital of the N atom. Thus, the excitation from the non-planar ground state into the planar triplet precursor causes the strong excitation of the umbrella inversion of NH_3. The rotational distributions of the departing fragments are selectively enhanced during subsequent bond-dissociation process. This gives rise to the breakdown of the assumption of the microcanonical distribution.

Formation of NH(A) from HN_3 and HNCO. The molecular structures of the ground state of HN_3[17] and HNCO[18] are trans bent in equilibrium (point group C_s). On the basis of CNDO/S study, we reported[8,9] that the precursor forming NH(A) from HN_3 and HNCO is presumably the $2^3A''$ state corresponding to excitation out of the 9a′ MO into the 3a″ MO. This result for HN_3 is supported by *ab initio* study.[19]

The observed rotational distributions of the $v=0$ level of NH(A) from HN_3 depend on the impact energy, while those from HNCO is independent of the impact energy. In HN_3, the values near the onset are compared with those predicted since the foregoing energy dependence is due to two different channels for formation of NH(A).

In the previous report for HNCO,[9] T_0 and P_1/P_0 are compared with those predicted by a simple statistical calculation based on the information theory.[20] This method assumes complete randomization of the available energy among all degrees of freedom in the products under the requirement of conservation of energy. The results predicted by use of $E_{av}=0.7$ eV show that the internal energy of NH(A) is selectively enhanced in the dissociation of the precursor state of HNCO. The present results show that the rotational distributions of NH(A) from HN_3 and HNCO are selectively enhanced much more than predicted by Method 2. Thus, the assumption of the microcanonical distribution cannot apply to Reactions 4 and 5. It can be concluded that the molecular structure of the $2^3A''$ precursor state of HN_3 and HNCO in equilibrium is fairly different from each ground state. For HN_3, Moore and Rosengren[21] found that the HN-NN stretch is strongly mixed with the H–N–N bend on the ground state. This suggests that the HN-NN stretching motion enhances the angular momentum of the separating $NH+N_2$ products when HN_3 dissociates.

Conclusion

On comparison of the observed and predicted internal energy distributions of NH(A), the assumption of the microcanonical distribution is found to be inapplicable to formation of NH(A) from NH_3, HN_3, and HNCO. The good agreement with the observed results is obtained by introduction of a coupling parameter, which represents the resonance feature in energy transfer process of the available energy. This result leads to selective excitation of the rotation of the fragments during bond-dissociation process.

Even if the phase space theory cannot be applied to the dissociation of such a small molecule, the internal energy distribution predicted can be used to estimate the mean available energy in electron-impact dissociation. Furthermore, this method including a nonstatistical bias can be used as a convenient criterion for prediction of whether the available energy is completely randomized among all the degrees of freedom in the products or a specific mode is enhanced.

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