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VIBRATIONAL OVERLAP INTEGRALS BETWEEN THE NEUTRAL AND ION STATES OF NH_3 AND ND_3: APPLICATION TO THE VIBRATIONAL DEPENDENCE OF THE $NH_3^+(v_2) + NH_3(0)$ SYMMETRIC CHARGE TRANSFER REACTION *

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ABSTRACT

Vibrational overlap integrals have been calculated for the transition between the neutral ground state and the ion state of NH_3 and ND_3 for the ν_2 vibrational bending mode. Calculations were performed by numerically solving the Schrödinger equation. The vibrational overlap integrals were used to simulate the dependence of the cross-section for the

$NH_3^+(v_2) + NH_3(0) \rightarrow NH_3(v_2'') + NH_3^+(v_2')$

symmetric charge-transfer reaction on the initial vibrational quantum state of the ion. The cross-sections show a gradual increase with v_2, in agreement with experiment.

INTRODUCTION

Many studies have been concerned with how the internal energy (or quantum state) of the reagent ion affects ion/molecule reaction cross-sections. Both resonance-enhanced multiphoton ionization (REMPI) [1–3] and photoion-photoelectron coincidence (PIPECO) [4–13] have shown that it is possible to conduct reactions with ions in specific vibrational quantum states. In particular, the ammonia ion has been a favorite system for studying the vibrational dependence of its ion/molecule reactions by these techniques owing to the relative ease with which NH_3^+ can be prepared in different vibrational levels [1–3,7,13].

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* Dedicated to Eldon E. Ferguson in honor of his contributions to ionic physics and chemistry.

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The structure of the neutral ammonia molecule in its ground electronic state was studied by Benedict and Plyler [14] and by Morino et al. [15]. The equilibrium N–H bond length was determined to be 1.0124 Å and the H–N–H angle to be 106.67°. Numerous single-photon vacuum ultraviolet photoelectron studies of ammonia have been reported [16]. Harshbarger [17] has calculated the Franck–Condon factors from $v = 0$ in the neutral ground state to the $\tilde{X}^2A_1''$ ion state in order to fit the observed photoelectron spectrum. He determined the structure of the ground state of the ion to be planar.

Many charge-transfer theories [8,18–25] have been developed based on calculations using Franck–Condon factors for transitions connecting the neutral and ion states. In this paper, we have evaluated the vibrational overlap integrals for the ν_2 bending mode between the neutral ground state and ion ground state of the ammonia molecule and have calculated the v_2 dependence of the

$$NH_3^+(v_2) + NH_3(0) \rightarrow NH_3(v_2'') + NH_3^+(v_2')$$

symmetric charge-transfer reaction cross-section. The calculations have been carried out for $v_2 = 0$ up to $v_2 = 5$ and include both resonant and non-resonant charge-transfer channels.

RESULTS AND DISCUSSION

Energy levels and vibrational overlap

The potential energy curve in the q_2 coordinate for the inversion mode is given by Harshbarger [17] as

$$V(q_2) = (k\rho^2)^{-1}\{-[b(b/2+1/2)\,\mathrm{sech}^2(y/2\rho)]/2 - D[\mathrm{sech}^2(y/2\rho) - \mathrm{sech}^4(y/2\rho)]\} \quad (1)$$

where $y = r_e(\pi/2 - \beta)$, $k = 8\pi^2 c\mu/h$, $\mu = 3m_H m_N/(3m_H + m_N)$, and β is the angle between the N–H bond and the threefold axis of symmetry. The values b, D, and ρ are empirically determined constants and these parameters are given in Table 1 for the neutral and ionic ground states of NH_3 and ND_3.

The calculation of the wavefunctions and eigenvalues appropriate to these potential curves has been performed using the method described by Cooley [26]. The vibrational energies for these potential curves together with the observed energies are listed in Table 2. The vibrational overlap integrals were evaluated by Simpson's formula and are listed in Table 3.

TABLE 1

Parameters for the ν_2 bending mode potential function

	NH_3		ND_3	
	Neutral	Ion	Neutral	Ion
b	87.7428	85.0	115.179	110.908
D	2809.543	1034.590	4806.581	1756.603
ρ (Å)	0.472305	0.45500	0.475023	0.45500
k (Å^{-2})	0.147538	0.147538	0.250500	0.250500

TABLE 2

Vibrational energies (cm^{-1}) of $NH_3(NH_3^+)$ and $ND_3(ND_3^+)$

The (+) and (−) refer to the symmetric and antisymmetric vibrational levels of the neutral.

v_2	NH_3					
	(+)		(−)		NH_3^+	
	Calc.	(Obs. [a])	Calc.	(Obs. [a])	Calc.	(Obs. [b,c])
0	0.00		0.83	(0.79)	0.00	
1	925	(933)	962	(968)	957	(968 [b], 944[c])
2	1593	(1598)	1876	(1910)	1930	(1855, 1888)
3	2380	(2384)	2891	(2896)	2918	(2823, 2904)
4	3458		4060		3918	(3872, 3888)
5	4697		5370		4929	(4921, 4872)
6	6044		6755		5950	(5890, 5952)
7	7486		8234		6978	(6938, 6912)
8	9001		9782		8014	(8067, 7969)

v_2	ND_3					
	(+)		(−)		ND_3^+	
	Calc.	(Obs. [a])	Calc.	(Obs. [a])	Calc.	(Obs. [b,c])
0	0.00		0.057	(0.053)	0.00	
1	742	(746)	746	(749)	721	(726 [b], 887[c])
2	1355	(1359)	1430	(1429)	1453	(1452, 1613)
3	1829	(1830)	2117	(2107)	2197	(2178, 2363)
4	2499	(2495)	2900		2951	(2904, 3234)
5	3333		3790		3714	(3630, 3903)
6	4269		4768		4486	(4356, 4694)
7	5285		5820		5265	(5162, 5339)
8	6371		6936		6052	(5889, 6146)

[a] Ref. 14.

[b] Ref. 29.

[c] Ref. 30.

TABLE 3

Vibrational overlap of ammonia molecule in the ν_2 bending mode [a]

NH_3^+ (v_2)	$NH_3(v_2)$								
	0	1	2	3	4	5	6	7	8
0	0.1418	−0.4951	0.7503	−0.3752	0.1296	−0.0423	0.0132	−0.004	0.0012
1	0.2712	−0.5789	0.6252	−0.3894	0.1766	−0.0682	0.024	−0.008	0.0026
2	0.406	−0.5431	−0.0779	0.5349	−0.4131	0.2135	−0.0917	0.0352	−0.0126
3	0.5135	−0.4348	−0.1598	0.5044	−0.4252	0.2423	−0.1129	0.0465	−0.0177
4	0.5759	−0.1665	−0.3655	−0.0748	0.4608	−0.4303	0.2651	−0.1319	0.0577
5	0.5852	0.051	−0.4111	−0.0397	0.4227	−0.4304	0.283	−0.149	0.0685
6	0.5434	0.2711	−0.0902	−0.395	0.0007	0.3873	−0.4268	0.2968	−0.1641
7	0.4669	0.4115	−0.0206	−0.3999	0.0335	0.3551	−0.4206	0.3072	−0.1773
8	0.370	0.4401	0.2677	−0.0325	−0.3963	0.061	0.326	−0.4127	0.3149
ND_3^+ (v_2)	$ND_3(v_2)$								
	0	1	2	3	4	5	6	7	8
0	0.0658	−0.2582	0.6618	−0.6358	0.2599	−0.0913	0.0305	−0.0098	0.003
1	0.1488	−0.4083	0.6273	−0.5429	0.3033	−0.1339	0.052	−0.0186	0.0063
2	0.2537	−0.5151	0.3586	0.3393	−0.5171	0.3386	−0.1689	0.0723	−0.0281
3	0.3642	−0.5303	0.1962	0.3378	−0.4936	0.3616	−0.1979	0.0916	−0.0038
4	0.4619	−0.4375	−0.1527	0.2626	0.2615	−0.4678	0.3765	−0.222	0.1095
5	0.5304	−0.2741	−0.3099	0.267	0.2107	−0.4417	0.3852	−0.2419	0.1259
6	0.5591	−0.0577	−0.3335	−0.201	0.2827	0.1627	−0.4155	0.3892	−0.2581
7	0.5461	0.1478	−0.3152	−0.2452	0.2953	0.1217	−0.3898	0.3897	−0.2711
8	0.4967	0.3143	−0.0886	−0.2912	−0.2281	0.3048	0.0863	−0.3652	0.3875

[a] Note that the symmetric (+) vibrational levels in the neutral state connect to even vibrational levels in the ion and the anti-symmetric (−) levels connect to odd vibrational levels.

$NH_3^+(v_2) + NH_3(0) \rightarrow NH_3(v_2'') + NH_3^+(v_2')$

The $NH_3^+(v_2) + NH_3(0) \rightarrow NH_3(v_2'') + NH_3^+(v_2')$ symmetric charge-transfer reaction was studied by Baer and Murray using the photoion-photoelectron coincidence technique [7]. They measured the vibrational dependence of the product ion and found that the reaction cross-section increases smoothly with vibrational excitation of the ν_2 mode of the reagent ion. The observed charge transfer cross-section is three times larger at $v_2 = 10$ (1.2 eV) than for $v_2 = 0$. However, for the two symmetric resonant reactions (in which the total number of vibrational quanta in the reactants is the same as in the products)

$$NH_3^+(0) + NH_3(0) \rightarrow NH_3(0) + NH_3^+(0) \qquad (2)$$

$$\Pi q_{v'v''} = 4.03 \times 10^{-4}$$

and

$$NH_3^+(5) + NH_3(0) \rightarrow NH_3(0) + NH_3^+(5) \tag{3}$$

$$\Pi q_{v'v''} = 0.117$$

where the product of the Franck–Condon factors, $\Pi q_{v'v''}$ for reaction (3) is 290 times bigger than for reaction (2). Thus, the results of Baer and Murray clearly indicate that non-resonant channels make the dominant contribution to this reaction.

The theoretical approach used to calculate the state-to-state cross-sections for symmetric charge-transfer reactions is based on the work of Bates and Reid [19] and of Moran and co-workers [21] who introduced the multistate impact parameter model. The model uses the time-dependent Schrödinger equation for the internal vibrational motion and classical trajectories for the relative translational motion. This treatment has been extended by DePristo [24,25]. The results of DePristo show excellent agreement with the exact quantal calculations of Becker [23] on the $O_2^+ + O_2$ symmetric charge-transfer system.

In the multistate impact parameter model, the time dependence of the internal motion of the system under the influence of the interaction potential $V(R)$ is given by

$$\psi(t) = \sum_{n=1}^{N} C_n(t)\Phi_n(r)\exp(-iE_n t) \tag{4}$$

where $\Phi_n(r)$ are the unperturbed molecular eigenfunctions (including the electronic, vibrational, and rotational parts for both the direct and the charge-transfer channels) for NH_3^+ and NH_3 at infinite center-of-mass separation R with energies E_n. Substitution of the wave function (4) into the time-dependent Schrödinger equation gives the following set of differential equations for the coefficients C_n.

$$i\frac{\partial C_i(t)}{\partial t} = \sum_{j=1}^{N} V(R)P_{ij}C_j(t)\exp\left[i(E_i - E_j)t\right] \tag{5}$$

with the boundary condition that one specific direct channel is initially populated. The matrix elements P_{ij} are equal to the product of the vibrational overlap integrals $\langle v_2^j(NH_3^+) \mid v_2^i(NH_3)\rangle \ \langle v_2^j(NH_3) \mid v_2^i(NH_3^+)\rangle$. These differential equations are solved together with the classically energy-conserving trajectory given by the equations

$$\frac{\partial R}{\partial t} = \frac{P}{\mu} \tag{6}$$

$$\frac{\partial P}{\partial t} = -\sum_i \sum_j C_j^* C_i \ \nabla_R V_{ji}(R)\exp\left[i(E_i - E_j)t\right] \tag{7}$$

for a given impact parameter b. The z-axis is taken as the direction of the initial velocity and perpendicular to the impact parameter. The square of the final value $C_f(\infty)$ gives the state-to-state reaction probability for each channel for a given impact parameter. The state-to-state reaction cross-sections are obtained via

$$\sigma(f \leftarrow i) = 2\pi \int_0^\infty b\,|C_f(\infty)|^2\,\mathrm{d}b \tag{8}$$

These complex differential equations can be rewritten as $2N+6$ real equations. They are solved by a variable step size Adams–Moulton integrator supplied with the IMSL routine DGEAR [27]. The interaction potential is

$$V = \begin{cases} D_0\{1/4\exp[-2\beta(R-R_e)] - 3/2\exp[-\beta(R-R_e)]\} & R > R^* \\ 0 & R < R^* \end{cases} \tag{9}$$

for the exchange channel, and

$$V = \begin{cases} D_0\{3/4\exp[-2\beta(R-R_e)] - 1/2\exp[-\beta(R-R_e)]\} & R > R^* \\ D_0\{\exp[-2\beta(R-R_e)] - 2\exp[-\beta(R-R_c)]\} & R < R^* \end{cases} \tag{10}$$

for the direct channel, where $R^* = R_e - \beta^{-1}\ln 6$.

The parameters D_0, R_e, and β are determined by fitting the Morse (gerade) function to the Lennard–Jones 12-6-4 potential.

$$V_{\mathrm{LJ4}} = 4\epsilon\left[(d/R)^{12} - (d/R)^6\right] - \alpha\,e^2/2R^4 \tag{11}$$

The parameters of Eq. (11) for the $NH_3^+ + NH_3$ system were obtained by Singh and Gupta [28] and the values for the Morse potential from this procedure are $\beta = 1.6377$ Å^{-1}, $R_e = 3.4475$ Å, and $D_0 = 0.11454$ eV.

Our calculations were done using a VAX 11 computer with double precision arithmetic. To test the program, we first reproduced the $O_2^+(1) + O_2(0)$ charge-transfer results previously obtained by DePristo [25] to demonstrate the quantitative accuracy of the semiclassical energy conserving trajectory approach. We set the starting position ($t = -\infty$) to be -40.0 Å along the z-axis and this distance is large enough to meet the condition that the system is initially isolated. For each step, the maximum vibrational quantum deficit was taken to be $\Delta v_{\max} = 4$ in Eq. (5). Calculations were performed for every 0.25 Å impact parameter. The results of the direct-channel (elastic scattering) probability and exchange-channel (charge transfer) probability at 8 eV collision energy are shown in Fig. 1 and can be directly compared with the results of the quantum mechanical calculation reported by Becker [23]. The agreement is excellent.

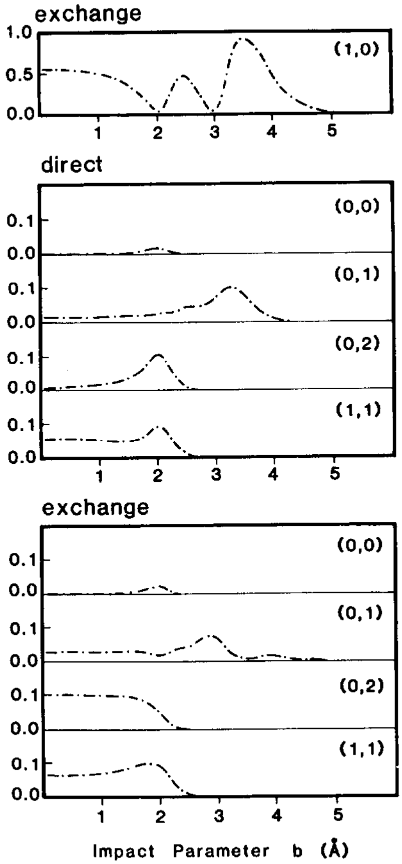

Fig. 1. Plot of the transition probability of the direct channel

$O_2^+(1)+O_2(0) \rightarrow O_2^+(v')+O_2(v'')$

and exchange channel

$O_2^+(1)+O_2(0) \rightarrow O_2(v'')+O_2^+(v')$

versus impact parameter at a center-of-mass collision energy of 8 eV. The numbers in parentheses represent (v', v'').

For the $NH_3^+(v_2) + NH_3(0)$ reaction, the calculation was performed at the center-of-mass collision energy of 10 eV to allow direct comparison with the experimental results reported by Baer and Murray [7]. Figure 2 shows the absolute value of the charge transfer (exchange) probability as a function of impact parameter for the ammonia ion initially populated in the $v_2 = 0$ state. The resonant charge transfer channel (2) is not a dominant channel and the reaction path is broadly distributed over the non-resonant channels. In the present model, the reaction pathways with large vibrational overlaps

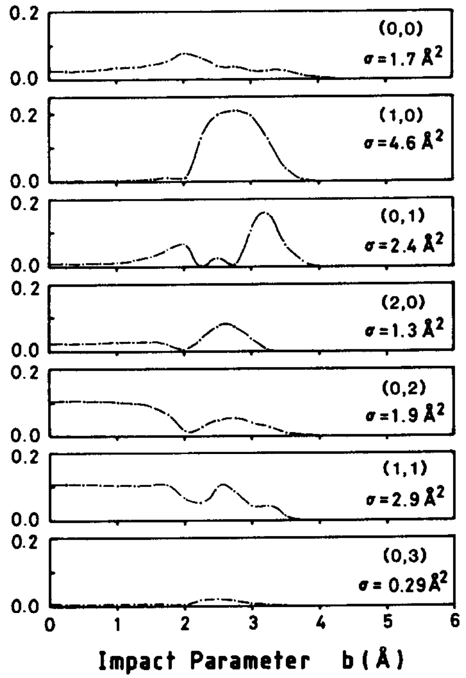

Fig. 2. Plot of the transition probability of the exchange channel versus impact parameter for the reaction

$$NH_3^+(0)+NH_3(0) \rightarrow NH_3(v_2'')+NH_3^+(v_2')$$

at a center-of-mass collision energy of 10 eV. The numbers in parentheses represent (v_2', v_2'').

and small energy defects with respect to the initial channel make the largest contribution to the cross-section. However, ammonia undergoes a large geometric change from the pyramidal neutral and ground state to the planar ion state, causing the Franck–Condon factors $|\langle NH_3^+(v_2')|NH_3(0)\rangle|^2$ to have a maximum value when $v_2' = 5$. Therefore, reaction (2) cannot be a major channel because the product of the vibrational overlap integrals is very small compared with the non-resonant channels. The large contribution by off-diagonal Franck–Condon factors distinguishes the symmetric ammonia charge transfer system from systems such as $O_2^+ + O_2$, $N_2^+ + N_2$, and $CO^+ + CO$ [21,23–25].

Figure 3 shows the relative probability for the formation of each charge transfer reaction product as a function of impact parameter. The numbers in each area denote the vibrational quantum numbers of the $NH_3^+(v_2')$ and $NH_3(v_2'')$. The state-to-state cross-sections to the charge-transfer channels are also given in Table 4. More than 94% of the products are populated in channels within $\Delta v_{total} = 3$. This is due to the fact that, for the channels with

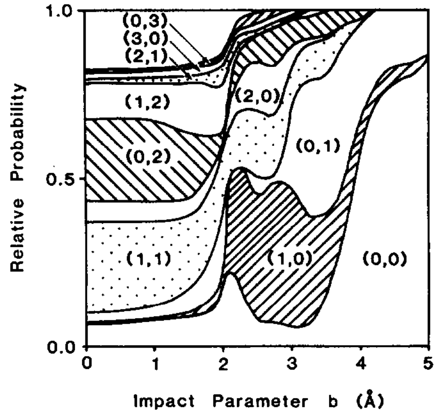

Fig. 3. Relative probability for specific charge-transfer products for the reaction NH_3^+ (0)+ NH_3(0) versus impact parameter at $KE_{c.m.} = 10$ eV. The numbers in parentheses represent (v_2', v_2'').

large energy deficits, the right-hand side of Eq. (5) oscillates rapidly and becomes very small. Therefore, the $\Delta v_{max} = 4$ assumption is sufficiently accurate to serve as the energy limit for these calculations.

Figure 4 shows the vibrational dependence of the total charge-transfer reaction cross-section for the $NH_3^+(v_2) + NH_3$ system. Although the calculated cross-sections are larger than the experimental results obtained by Baer and Murray [7], the relative vibrational dependence agrees well (see Table 5).

TABLE 4

State-to-state cross-sections for the

$NH_3(v_2)+NH_3(0) \rightarrow NH_3(v_2'')+NH_3^+(v_2')$

charge-transfer reaction at 10 eV center of mass kinetic energy

(v_2', v_2'')	Cross-section (Å^2)
(0, 0)	1.7
(1, 0)	4.6
(0, 1)	2.4
(1, 1)	2.9
(2, 0)	1.3
(0, 2)	1.9
(3, 0)	0.27
(0, 3)	0.29
(2, 1)	0.25
(1, 2)	0.87
Total	17.4

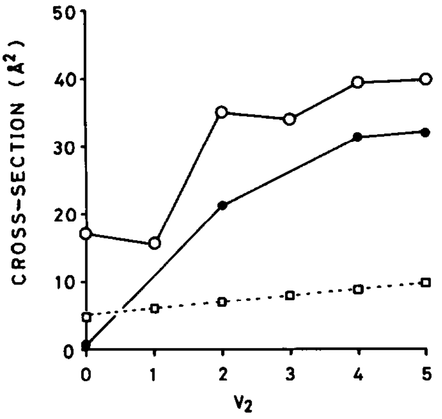

Fig. 4. Vibrational dependence of the total cross-section for the

$NH_3^+(v_2)+NH_3(0) \rightarrow NH_3(v_2'')+NH_3^+(v_2')$

exchange reaction at a center-of-mass collision energy of 10 eV. Calculated cross-sections: ○, $\Delta v_{max} = 4$; ●, $\Delta v_{max} = 0$. Experimental cross-sections (□) taken from Baer and Murray [7].

Figure 4 also shows the results of the calculation assuming $\Delta v_{max} = 0$. The reaction cross-section is found to increase very rapidly with v_2. This shows that, in the case of $\Delta v_{max} = 0$, the cross-section is mainly dominated by the $|\langle NH_3^+(v_2')|NH_3(0)\rangle|^2$ Franck–Condon factor and the disagreement with experiment comes from the large contribution of non-resonant channels to the symmetric charge-transfer process. The difference between the observed and the calculated absolute cross-sections may come partly from the fact that all the product ions could not be collected in the experiment and/or from the inaccuracy in the assumed gerade and ungerade potential func-

TABLE 5

Vibrational dependence of the relative cross-section of the

$NH_3^+(v_2)+NH_3(0) \rightarrow NH_3(v_2'')+NH_3^+(v_2')$

charge-transfer reaction

v_2	Experimental [a]	Calculated
0	1.0	1.0
1	1.2	0.91
2	1.4	2.0
3	1.6	2.1
4	1.8	2.4
5	2.0	2.5

[a] Ref. 7.

tions. The limitations in the present calculation may be that the molecular orientation dependence in the interaction potential has been neglected, or in the assumption that the Sato anti-Morse potential form is sufficiently adequate to describe the charge-exchange interaction potential. In his later work, DePristo [25] performed several calculations for the $O_2^+(v) + O_2$ charge transfer reaction by reducing the charge-exchange interaction potential [Eq. (9)] to obtain better quantitative agreement with the experimental results [6]. We have not performed a similar treatment in the present calculations because of the unclear physical meaning of reducing the exchange interaction potential.

In conclusion, we have evaluated the vibrational overlap integrals for the ν_2 bending mode between the neutral and ion states of the ammonia molecule and have used them to calculate the v_2 vibrational dependence of the

$$NH_3^+(v_2) + NH_3(0) \rightarrow NH_3^+(v_2') + NH_3(v_2'')$$

symmetric charge-transfer reaction cross-section. The results indicate that the product ions are spread over a large number of vibrational levels and the vibrational dependence of the calculated relative reaction cross-sections agrees favorably with experimental results.

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