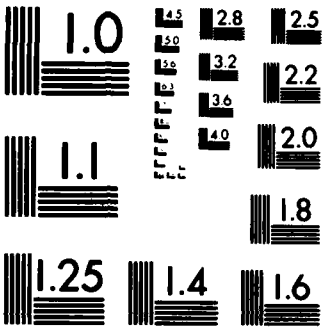
AD-A150 068 STATE-SELECTED ION-MOLECULE REACTION DYNAMICS(U) 1/1
STANFORD UNIV CA DEPT OF CHEEISTRY R J MORRISON ET AL.
15 DEC 84 AFOSR-TR-84-1238 F49620-83-C-0033

UNCLASSIFIED F/G 7/5 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

FINAL REPORT

STATE-SELECTED ION-MOLECULE REACTION DYNAMICS

RICHARD N. ZARE

F49620-83-C-0033

DEPARTMENT OF CHEMISTRY

STANFORD UNIVERSITY

STANFORD, CA 94305

1 NOVEMBER 1982-31 OCTOBER 1984

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A150068

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): AFOSR F49620-83-C-0033	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFOSR-TR- 84 1238
6a. NAME OF PERFORMING ORGANIZATION: Professor Richard N. Zare; 6b. OFFICE SYMBOL (If applicable):	7a. NAME OF MONITORING ORGANIZATION: NFOSR/NC
6c. ADDRESS (City, State and ZIP Code): Department of Chemistry, Stanford University, Stanford, CA 94305	7b. ADDRESS (City, State and ZIP Code): Bldg. 410, Bolling AFB, DC 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR; 8b. OFFICE SYMBOL (If applicable): NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: F49620-83-C-0033
8c. ADDRESS (City, State and ZIP Code): Bldg 410, Bolling AFB, DC 20332-6448	10. SOURCE OF FUNDING NOS. — PROGRAM ELEMENT NO.: 61102F; PROJECT NO.: 2303; TASK NO.: B1; WORK UNIT NO.:
11. TITLE (Include Security Classification): State-Selected Ion-Molecule Reaction Dynamics	
12. PERSONAL AUTHOR(S): Richard J.S. Morrison, William E. Conaway, and Richard N. Zare	
13a. TYPE OF REPORT: Final; 13b. TIME COVERED: FROM 11/01/82 TO 10/31/84	14. DATE OF REPORT (Yr., Mo., Day): December 15, 1984; 15. PAGE COUNT: 6
16. SUPPLEMENTARY NOTATION: The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army/A.F. position, policy, or decision	
17. COSATI CODES — FIELD / GROUP / SUB GR.	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

By analyzing the photoelectron energies in several systems, it has been demonstrated that multiphoton ionization (MPI) can selectively produce molecular ions predominantly in a single vibrational level by the proper choice of the laser wavelength employed. Thus, MPI provides a powerful new technique for producing high densities of internally state-selected reagent ions for chemical reaction dynamics studies. This approach is being taken for studying the ion-molecule reactions of $NH_3^{(+)}(v)$ which has been prepared with v = 0-9 vibrational quanta in the ν_2 umbrella-bending mode.

nu sub 2

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION: Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: LEE E. NIVERS, CAPT, USAF	22b. TELEPHONE NUMBER (Include Area Code): (202) 767-4963; 22c. OFFICE SYMBOL: NC

DD FORM 1473, 83 APR — EDITION OF 1 JAN 73 IS OBSOLETE.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

STATE-SELECTED ION-MOLECULE REACTION DYNAMICS

Richard J.S. Morrison, William E. Conaway, and Richard N. Zare
Department of Chemistry, Stanford University
Stanford, California 94305

December 15, 1984

By analyzing the photoelectron energies in several systems, it has been demonstrated that multiphoton ionization (MPI) can selectively produce molecular ions predominantly in a single vibrational level by the proper choice of the laser wavelength employed. Thus, MPI provides a powerful new technique for producing high densities of internally state-selected reagent ions for chemical reaction dynamics studies. This approach is being taken for studying the ion-molecule reactions of $NH_3^+(v)$ which has been prepared with $v = 0$-9 vibrational quanta in the ν_2 umbrella-bending mode.

The experimental arrangement consists of a 2+1 laser multiphoton ion source and an ion optics system for controlling the kinetic energy of the reactant ion beam. A constant pressure of the target neutral species is maintained in a field-free collision cell. Forward-scattered products and unreacted primary ions are collected and analyzed by a quadrupole mass spectrometer and detection electronics. The mass signal as a function of the reaction cell potential (primary ion translational energy) and of the laser wavelength (primary ion vibrational energy) is then recorded by the data acquisition system.

Two reaction products have been observed from the reaction of $NH_3^+ + D_2$.

$$NH_3^+ + D_2 \rightarrow NH_3D^+ + D \qquad (1)$$

$$NH_3^+ + D_2 \rightarrow NH_2D^+ + HD \qquad (2)$$

The D atom abstraction channel to form NH_3D^+ is slightly exothermic while the D atom exchange channel to form NH_2D^+ is thermoneutral (Figure 1). We

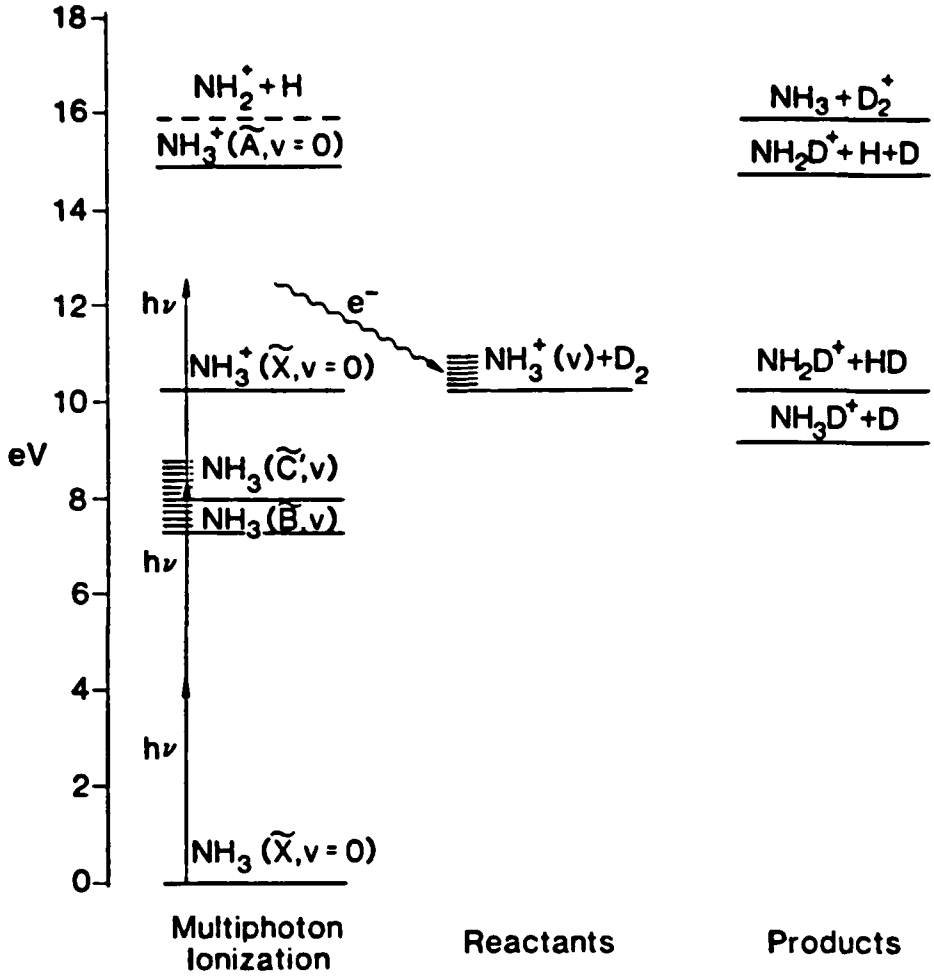


Figure 1

observe the former channel to dominate over the NH_3^+ translational energy range examined (1 - 10 ev in the center of mass frame). A sharp decrease in the NH_3D^+ yield is found above an energy corresponding closely to the HD bond strength. This decrease is correlated with an increase in the NH_2D^+ product signal (Figure 2a). These results can be attributed to the onset of a third reaction channel

$$NH_3^+ + D_2 \longrightarrow NH_3D^{*+} + D \longrightarrow NH_2D^+ + H + D \quad (3)$$

in which the NH_2D^+ is produced by unimolecular decomposition of the NH_3D^+ ion formed in Reaction 1 with excess internal energy.

Owing to the implicit lack of control over the ion internal states in previous studies, nothing could be said about the the influence that vibra-

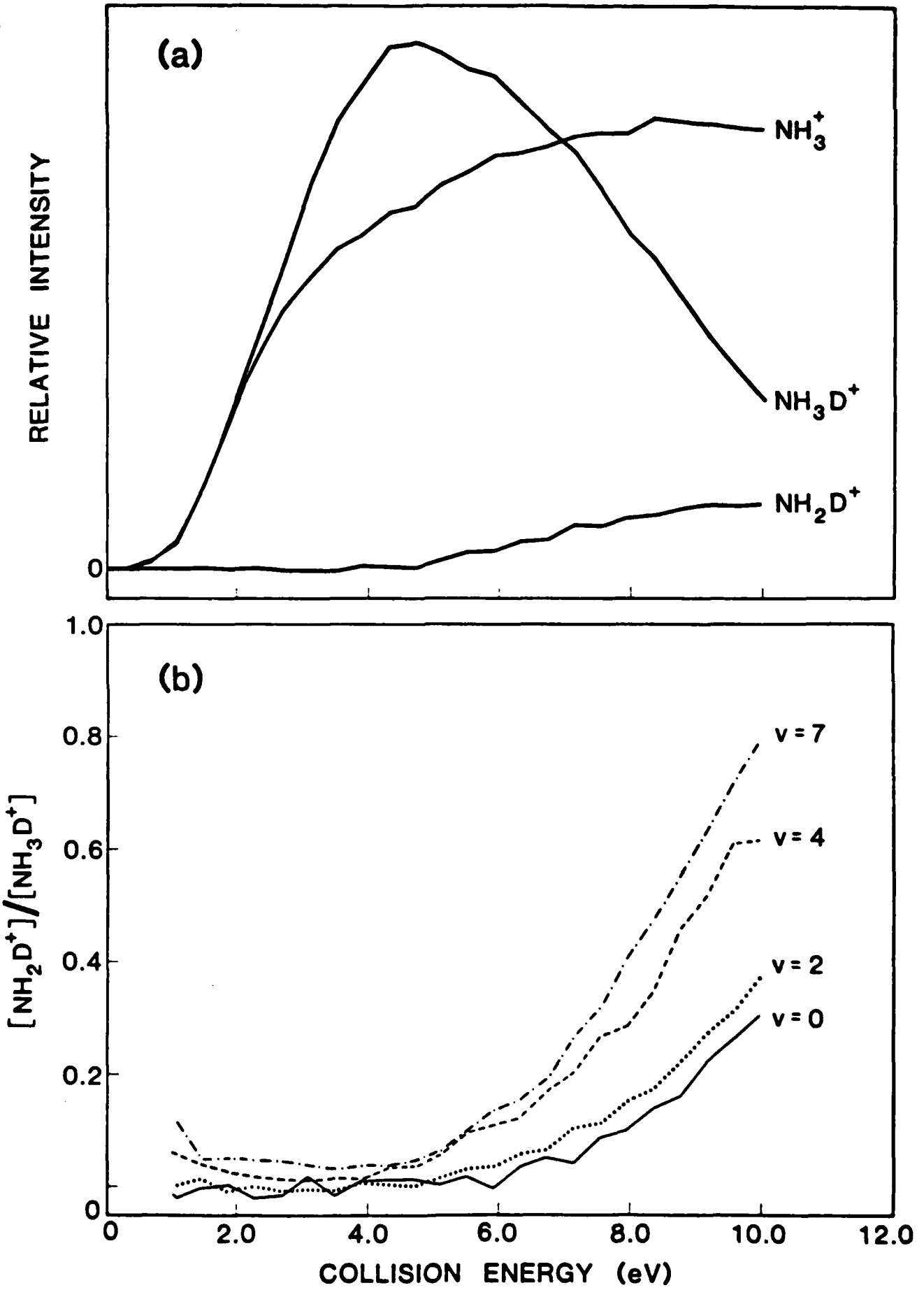

(a)
RELATIVE INTENSITY
NH_3^+
NH_3D^+
NH_2D^+
0
(b)
$[NH_2D^+]/[NH_3D^+]$
1.0
0.8
0.6
0.4
0.2
0
v = 7
v = 4
v = 2
v = 0
0
2.0
4.0
6.0
8.0
10.0
12.0
COLLISION ENERGY (eV)

Figure 2

tion (and rotation) has on the reaction of ammonia ions with H_2 and D_2. By developing the laser MPI technique for preparing state-selected ions, it has now become possible to examine this reaction in much greater detail. We find that within our experimental uncertainty, the addition channel (Reaction 1) is not influenced by vibrational excitation. This is not unexpected as, in general, internal energy does not play a significant role in exothermic reactions. However, we do observe a significant vibrational effect on the exchange channel (Reactions 2 and 3). Vibrational excitation of the ammonia ion appears to enhance this channel producing more NH_2D^+ for the higher vibrational excitation of the NH_3^+ reagent ion.

Plotted in Figure 2b is the branching ratio, defined by NH_2D^+/NH_3D^+, versus the NH_3^+ reagent ion collision energy for several NH_3^+ vibrational states. The effect of vibration is particularly evident in the higher energy region where increasing the internal energy promotes the formation of $NH_2D^+ + H$ (as well as $NH_3^+ + D$ which is not detectable) at the expense of NH_3D^+. If one assumes a spectator stripping model for this reaction, 55 % of the NH_3^+ kinetic energy is carried into internal excitation of the NH_3D^+. When the total internal energy of the NH_3D^+ is taken into account, including the initial vibrational excitation of the $NH_3^+(v)$ which is retained in the NH_3D^+, the spacing of the data curves for the different vibrational quanta is less pronounced. This indicates that at high collision energy, the total internal energy of the NH_3D^+ formed by Reaction 1 is the predominant factor in determining the amount of NH_2D^+ produced. There also appears to be some vibrational influence at low collision energy where Reaction 3 cannot occur and Reaction 2 becomes the dominate exchange pathway. Vibrational effects arising from dyanmical considerations are most likely to be found here. This low energy regime will be studied more closely in future experiments.

It is not intuitively obvious how the umbrella-bending motion of the NH_3^+ ion couples to the reaction coordinate for this reaction. The approach of the D_2 is most certainly out of the plane formed by three ammonia hydrogens since the lone electron on the nitrogen projects out along the C_3 axis. Vibration along this axis effects both the electron density distribution and the steric hinderance caused by the ammonia hydrogens. This symmetric bending motion must also map over into the vibrational modes of the tetrahedral NH_3D^+ system. Calculation of the $NH_3^+ + H_2$ potential energy surface would greatly aid the understanding of the dynamics of this class of reactions.

END

FILMED

3-85

DTIC