

- ⁹Research supported by the National Science Foundation, Grant No. CHE-8205769.
- ¹D. G. Truhlar and R. E. Wyatt, *Annu. Rev. Phys. Chem.* **21**, 1 (1976).
- ²P. Siegbahn and B. Liu, *J. Chem. Phys.* **68**, 2457 (1978); D. G. Truhlar and C. J. Horowitz, *ibid.* **68**, 2468 (1978); **71**, 1514(E) (1979).
- ³For a review and bibliography, see G. C. Schatz, in *The Theory of Chemical Reaction Dynamics*, edited by D. C. Clary (Reidel, Dordrecht, 1986), Chap. 1.
- ⁴D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* **81**, 1298 (1984); **82**, 1323 (1985); **83**, 2207 (1985).
- ⁵E. E. Marinero, C. T. Rettner, and R. N. Zare, *J. Chem. Phys.* **80**, 4142 (1984); C. T. Rettner, E. E. Marinero, and R. N. Zare, in *Physics of Electronic and Atomic Collisions*, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (North-Holland, Amsterdam, 1984), p. 51.
- ⁶(a) K. Tsukiyama, B. Katz, and R. Bersohn, *J. Chem. Phys.* **84**, 1934 (1986); (b) U. Gerlach-Mayer, K. Kleinermanns, G. Linnebach, and J. Wolfrum, *J. Chem. Phys.* **86**, 3047 (1987).
- ⁷G. C. Schatz, *Chem. Phys. Lett.* **108**, 532 (1984).
- ⁸N. C. Blais and D. G. Truhlar, *Chem. Phys. Lett.* **102**, 120 (1983).
- ⁹S. Datz and E. H. Taylor, *J. Chem. Phys.* **39**, 1896 (1963).
- ¹⁰J. Geddes, H. F. Krause, and W. L. Fite, *J. Chem. Phys.* **56**, 3298 (1972).
- ¹¹G. H. Kwei and V. W. S. Lo, *J. Chem. Phys.* **72**, 6265 (1980).
- ¹²R. Götting, H. R. Mayne, and J. P. Toennies, *J. Chem. Phys.* **80**, 2230 (1984); **85**, 6396 (1986).
- ¹³W. R. Gentry and C. F. Giese, *J. Chem. Phys.* **67**, 5389 (1977); *Phys. Rev. Lett.* **39**, 1259 (1977); *Rev. Sci. Instrum.* **49**, 595 (1978).
- ¹⁴M. A. Hoffbauer, S. Burdinski, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **78**, 3832 (1983).
- ¹⁵M. A. Hoffbauer, K. Liu, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **78**, 5567 (1983).
- ¹⁶W. R. Gentry, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University, Oxford, in press), Chap. 3.
- ¹⁷All resolution parameters quoted refer to the full widths at half-maximum.
- ¹⁸G. Hall, K. Liu, M. J. McAuliffe, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **84**, 1402 (1986).
- ¹⁹R. B. Bernstein and R. D. Levine, *Acc. Chem. Res.* **7**, 393 (1974).

Two-dimensional imaging of state-selected photodissociation products detected by multiphoton ionization^{a)}

David W. Chandler

Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550

Paul L. Houston

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

(Received 9 April 1987; accepted 12 May 1987)

Many problems in molecular dynamics demand the simultaneous measurement of internal energy and velocity. Consider the case of a photodissociation that produces two fragments, AB and CD. Even if the internal energy distribution of the AB and CD fragments were each measured separately, it would still be necessary to obtain information on the recoil speed in order to determine which levels of the AB fragment were generated in coincidence with given states of the CD fragment. The recoil angle, with respect to the polarization vector of the dissociating light, gives additional information about the transition moment in the parent molecule and the time scale of dissociation. Although the earliest photofragment spectrometers measured either the recoil velocity distribution^{1,2} or the internal energy of the fragments,^{3,4} it has only been recently that a Doppler technique has been developed to obtain the correlation between these properties.⁵⁻⁷ In this paper we present a technique in which the three-dimensional spatial distribution of a photofragment, measured at a set time after photodissociation, is projected onto a two-dimensional surface. Our method offers advantages over a recently reported optical imaging technique⁸ in that the detection is mass specific and the sensitivity and spatial resolution are much higher. The method is applied here to the photodissociation of CH₃I.⁹⁻²³ CH₃I dissociates into two channels leading to either methyl radical plus electronically excited iodine, I(²P_{1/2}) + CH₃, or methyl radical plus ground state iodine, I(²P_{3/2}) + CH₃. For dissociation at 266 nm, the fraction leading to I(²P_{1/2}) is about 0.8. The ground state CH₃ fragment generated in coincidence with the ground state I(²P_{3/2}) channel has approximately 1.3

times the velocity as the ground state CH₃ generated in coincidence with I(²P_{1/2}).

We form a molecular beam of CH₃I/He by flowing He at 25 psi over CH₃I at 0°C and then flowing the mixture through a pulsed nozzle. The pulsed beam is skimmed and directed into the imaging ion detector through a hole in a repeller plate. An unfocused, quadrupled Nd:YAG laser beam (266 nm) intersects the molecular beam at right angles and dissociates the CH₃I. A focused (12 cm f.l. lens), counterpropagating, doubled-dye-laser beam (wavelength near 330 nm) intersects the fragments 10 ns later and ionizes CH₃(*v* = 0) via 2 + 1 multiphoton ionization on the 0-0 band of the 3P²(A₂^{''}) ← 2P²(A₂^{''}) transition.²⁴ The state-selected ions are created between the repeller (0-200 V) and a pair of grounded grids mounted in front of the imaging detector and separated from the repeller by 7.5 cm. Another screen, which is used as an ion shutter, is located between the grounded screens and the ion detector. This screen remains at ground potential until the CH₃⁺ passes, and it then is switched positive (250 V) to repel any CH₃I⁺ ions or high-molecular-weight background ions. The position of each ion is recorded with a combination microchannelplate/phosphor screen detector. The images are detected by either polaroid film (ASA 3000, 4 min. exposure) or a two-dimensional intensified reticon array. By using the photomultiplier tube (1P28) to detect the ions, we determine the arrival time of the CH₃⁺, thereby allowing us to set the timing of the voltage pulse to the ion shutter. The maximum velocity of the fragments is directly determined from the measured position and arrival time. In order to obtain an accurate deter-

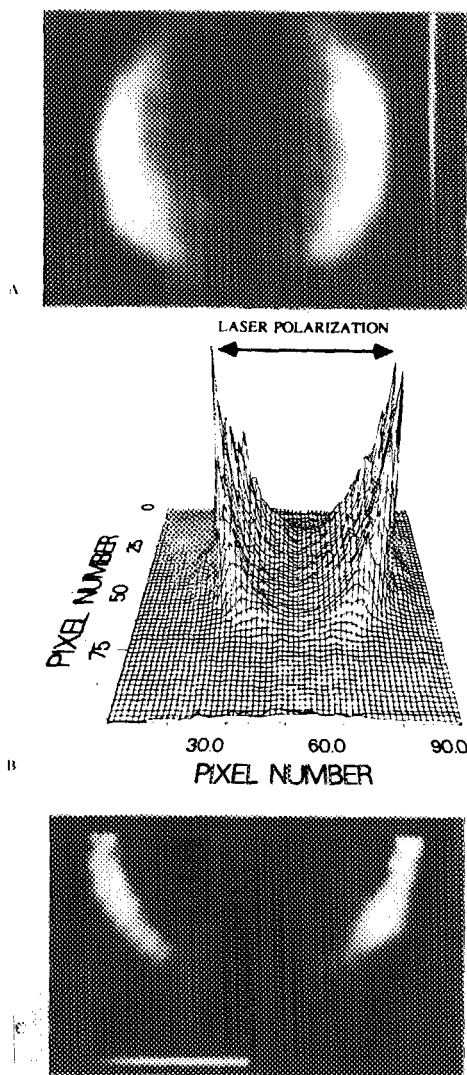


FIG. 1. (a) Image produced by projecting onto two dimensions the three-dimensional spatial distribution of $\text{CH}_3(v=0)$ fragments produced from photolysis of CH_3I with 266 nm laser light. The plane of the projection is parallel to the polarization axis of the 266 nm laser beam. The ion intensity is represented by a continuous grey scale (white being highest intensity). (b) Intensity plot of the data of (a). A faint outer ring and an intense inner ring are clearly seen, corresponding to the two possible dissociation channels. (c) Reconstructed cross section of the three-dimensional spatial distribution of $\text{CH}_3(v=0)$ fragments necessary to produce the two-dimensional projection of (a).

mination of the intensity variation over the image, a two-dimensional intensified reticon array was used to record the image. The detector has a sensor containing approximately 90×100 pixels, each with a dynamic range of about 100. We typically average 50 images taken with the same conditions.

Figures 1(a) and 1(b) shows the image of the $\text{CH}_3(v=0)$ fragments for alignment of the polarization of the dissociation laser parallel to the detector face. We obtain the distribution of photofragments, at a fixed time delay

after dissociation, by reconstructing the three-dimensional "ion cloud" that gave rise to the two-dimensional image, Fig. 1(c). From inspection of the image, the nature of the dissociation event can be seen directly. The \cos^2 dependence in the intensity pattern indicates a parallel transition accompanied by prompt dissociation. Rotation about the top axis of Fig. 1(c) will regenerate the entire 3D distribution.

The problem of reconstructing a three-dimensional function from a two-dimensional projection has been considered extensively.²⁵⁻²⁷ When the 3D object is cylindrically symmetric, one 2D projection taken parallel to the polarization axis is sufficient for complete determination of the 3D function.²⁸ A double ring is obtained in the reconstruction, although the outer ring is not visible in Fig. 1(c) due to its weakness. The relative intensities indicate that greater than 95% of the $\text{CH}_3(v=0)$ fragments are formed in coincidence with $I(^2P_{1/2})$. This is in contrast to the percentage¹⁰ (80%) found when the measurement is made over the average of all the vibrational states of the CH_3 , but is consistent with the modeling of the time-of-flight measurements.^{13,19}

Presently, the main limitation to the spatial resolution of the projection is due to the fact that the molecular beam width is significant on the scale of the image. This effect can be minimized by crossing the two laser beams at 90° .

It should be emphasized that the imaging technique described above is applicable to a wide range of chemical problems. This technique is easily generalizable to the detection of products in crossed molecular beams, where acceleration of the state-selected fragment ions in any direction perpendicular to the relative velocity vector will provide a projection from which the full three-dimensional velocity distribution can be reconstructed (i.e., a state-selective Newton diagram).

In conclusion, we have shown that it is possible to record, at one time, the entire spatial distribution of a state-selected photofragment in such a manner that both its angular and speed distribution are determined. This technique gives us direct information on the dynamics and time scale of the photodissociation event.

¹ Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

² G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, *J. Chem. Phys.* **51**, 449 (1969); R. W. Diesen, J. C. Wahr, and S. E. Adler, *ibid.* **50**, 3635 (1969).

³ M. Dzvonič, S. Yang, and R. Bersohn, *J. Chem. Phys.* **61**, 4408 (1974).

⁴ W. M. Jackson, *J. Chem. Phys.* **59**, 960 (1973); W. M. Jackson and R. J. Cody, *ibid.* **61**, 4183 (1974).

⁵ A. P. Baronavski and J. R. McDonald, *Chem. Phys. Lett.* **45**, 172 (1977).

⁶ J. L. Kinsey, *J. Chem. Phys.* **66**, 2560 (1977).

⁷ R. Schmiedl, H. Dugan, W. Meier, and K. H. Welge, *Z. Phys. A* **304**, 137 (1982).

⁸ Y. Nadler, D. Mahgerefteh, H. Reisler, and C. Wittig, *J. Chem. Phys.* **82**, 3385 (1985).

⁹ D. Eres, M. Grunick, and J. D. McDonald, *J. Chem. Phys.* **81**, 5552 (1984).

¹⁰ J. V. V. Kasper and G. C. Pimentel, *Appl. Phys. Lett.* **5**, 231 (1964).

¹¹ S. J. Riley and K. R. Wilson, *Discuss. Faraday Soc.* **53**, 132 (1972).

¹² M. J. Dzvonič and S. C. Yang, *Rev. Sci. Instrum.* **45**, 750 (1974).

¹³ S. L. Baughcum and S. R. Leone, *J. Chem. Phys.* **72**, 6531 (1980).

- ¹³R. K. Sparks, K. Shobatake, L. R. Carlson, and Y. T. Lee, *J. Chem. Phys.* **75**, 3838 (1981).
- ¹⁴M. Shapiro and R. Bersohn, *J. Chem. Phys.* **73**, 3810 (1980); K. Tsukiyama, B. Katz, and R. Bersohn, *Chem. Phys. Lett.* **124**, 309 (1986); M. Shapiro, *J. Phys. Chem.* **90**, 3644 (1986).
- ¹⁵S. K. Gray and M. S. Child, *Mol. Phys.* **51**, 189 (1984).
- ¹⁶S. Lee and E. J. Heller, *J. Chem. Phys.* **76**, 4766 (1982).
- ¹⁷Y. Jiang, M. R. Giorgi-Arnazzi, and R. B. Bernstein, *Chem. Phys.* **106**, 171 (1986).
- ¹⁸H. W. Hermann and S. R. Leone, *J. Chem. Phys.* **76**, 4759 (1982).
- ¹⁹G. N. A. van Veen, T. Baller, A. E. de Vries, and N. J. A. van Veen, *Chem. Phys.* **87**, 405 (1984).
- ²⁰M. D. Barry and P. A. Gorry, *Mol. Phys.* **52**, 461 (1984).
- ²¹A. M. Woodward, S. D. Colson, W. A. Chupka, and M. G. White, *J. Phys. Chem.* **90**, 274 (1986).
- ²²A. Gedanken and M. D. Rowe, *Chem. Phys. Lett.* **34**, 39 (1975).
- ²³D. Imre, J. L. Kinsey, A. Sinha, and J. Krenos, *J. Phys. Chem.* **88**, 3956 (1984); M. O. Hale, G. E. Galica, S. G. Glogover, and J. L. Kinsey, *ibid.* **90**, 4997 (1986).
- ²⁴J. W. Hudgens, T. G. DiGiuseppe, and M. C. Lin, *J. Chem. Phys.* **79**, 571 (1983).
- ²⁵D. J. DeRosier and A. Klug, *Nature* **217**, 130 (1968).
- ²⁶M. Zwick and E. Zeitler, *Optik* **38**, 550 (1973).
- ²⁷L. A. Shepp and B. F. Logan, *IEEE Trans. Nucl. Sci.* **NS-21**, 21 (1974).
- ²⁸K. R. Castleman, *Digital Image Processing* (Prentice-Hall, Englewood Cliffs, 1979), pp. 184–185.

Vibronic energy distribution of H_2O^+ produced in charge transfer scattering of D^+ by H_2O

Bretislav Friedrich,^{a)} Gereon Niedner, Martin Noll, and J. Peter Toennies
Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen, Federal Republic of Germany

(Received 31 March 1987; accepted 12 May 1987)

Charge transfer collisions of molecules with ions provide a sensitive test of the current understanding of the nonadiabatic coupling of electronic and vibrational degrees of freedom.¹ Except for recent experiments with diatomic reactant molecules,² in most previous charge transfer scattering studies only the product electronic states could be distinguished. In this Communication we report a crossed beam study on the charge transfer between deuterons and water molecules, a system of great chemical and biological interest where, for the first time, individual vibronic states of a triatomic molecular ion produced in charge transfer collisions were resolved.

In the present experiment the scattered D atoms were detected by an open CuBe electron multiplier (detection efficiency of 1%) and their time-of-flight (TOF) spectra at different laboratory scattering angles $0 < \theta < 8^\circ$ and collision energies $30 < E_{\text{CM}} < 50$ eV were measured; for experimental details, cf. Ref. 2 (a). By conservation of energy, the TOF spectra provide direct information on the final state distribution of the H_2O^+ molecular ions formed. One of the best-resolved TOF spectra of the D atoms, converted to $\Delta E_{\text{CM}} \equiv E'_{\text{CM}} - E_{\text{CM}}$ to indicate the net change of the relative translational energy, is shown in the lower part of Fig. 1 [$E_{\text{CM}} = 30.1$ eV, $\theta = 1^\circ$, effective energy resolution of 90 meV (FWHM)]. Two bands can be distinguished in the spectrum with their edges positioned at $\Delta E_{\text{CM}} \approx -1.0$ and 0.2 eV corresponding to the H_2O^+ electronic states with ionization potentials of about 12.6 and 13.8 eV, respectively (cf. the upper scale in Fig. 1). By comparing these values with the known ionization potentials, IP, of H_2O^+ ,³ the exo- and endoergic bands could be unequivocally assigned to the formation of H_2O^+ in the \tilde{X}^2B_1 and \tilde{A}^2A_1 electronic states, respectively; no evidence for the next higher electronic state

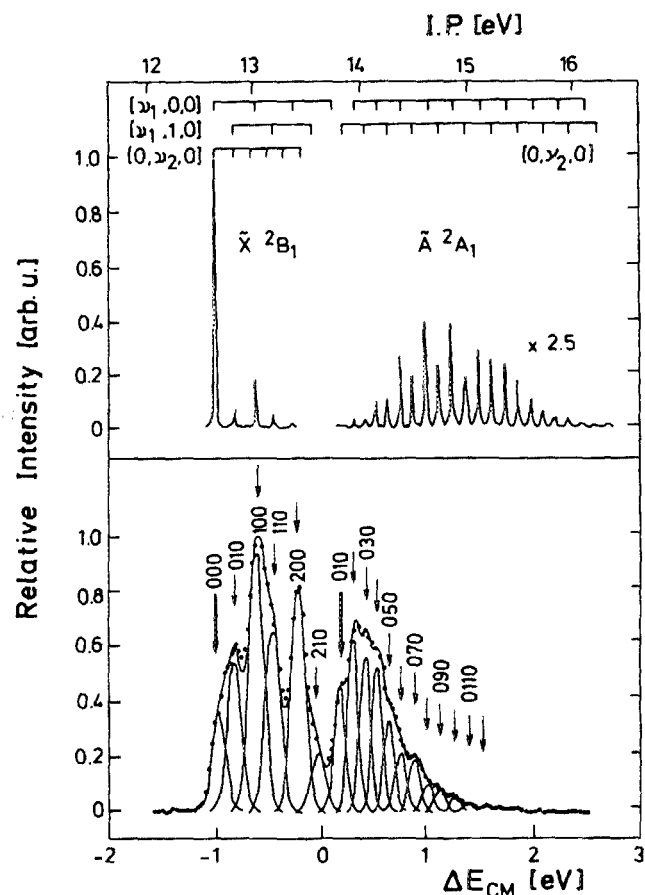


FIG. 1. Vibronic energy distributions of H_2O^+ as determined from time-of-flight spectra of the D atoms produced in $\text{D}^+ + \text{H}_2\text{O}$ charge transfer collisions at $E_{\text{CM}} = 30.1$ eV and $\theta = 1^\circ$ (lower part) and from photoionization of H_2O , Ref. 3 (upper part; only the first two bands are shown). The arrows indicate the assigned vibrational energy levels.