Lawrence Berkeley National Laboratory
Recent Work

Title

SYMMETRIC STRETCH EXCITATION OF CH[SUB]3 IN THE 193.3 NM PHOTOLYSIS OF CH[SUB]3 I

Permalink

https://escholarship.org/uc/item/7h054629

Authors

Continetti, R.E.
Balko, B.A.
Lee, Y.T.

Publication Date

1988-05-01

eScholarship.org Powered by the California Digital Library
University of California

LBL-25355 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JUL 26 1988
LIBRARY AND
DOCUMENTS SECTION

Materials & Chemical
Sciences Division

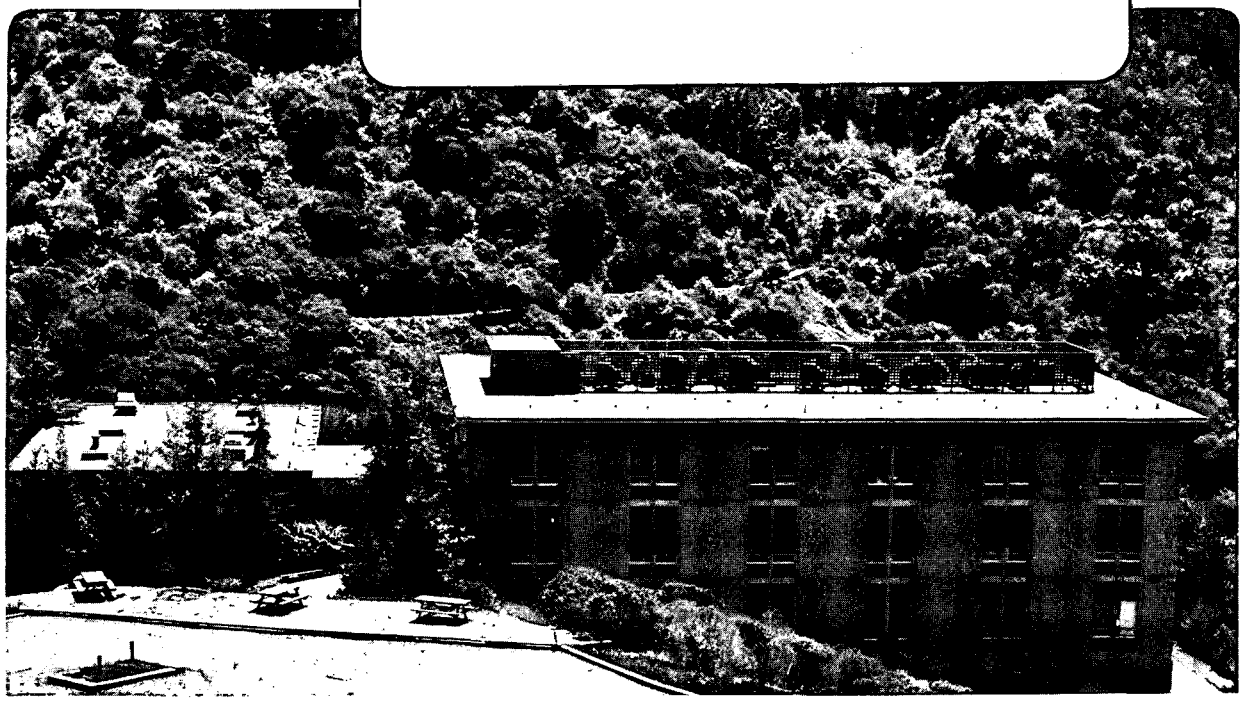
Submitted to Journal of Chemical Physics

Symmetric Stretch Excitation of CH_3 in the 193.3 nm Photolysis of CH_3I

R.E. Continetti, B.A. Balko, and Y.T. Lee

May 1988

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

LBL-25355
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-25355

Symmetric Stretch Excitation of CH_3 in the 193.3 nm Photolysis of CH_3I

R. E. Continetti, B. A. Balko, and Y. T. Lee,

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory
and
Department of Chemistry, University of California, Berkeley

Submitted to the Journal of Chemical Physics
May 27, 1988

PACS #'s: 33.80.Gj, 35.20.Gs, 31.60.+b

Abstract:

New high resolution photofragment translational spectroscopy measurements on the 193.3 nm photolysis of CH_3I reveal up to four quanta of υ_1 C-H symmetric stretch excitation in the C-I bond fission channel. In addition these experiments show for the first time that C-H bond fission occurs at wavelengths longer than 185 nm with a quantum yield of ca. 3%. The data yields upper bounds to the C-H bond dissociation energy in CH_3I of 101 ± 1 kcal/mol and for the C-I bond energy, 55.0 ± 0.3 kcal/mol.

The photodissociation dynamics of CH_3I has been studied in great detail in the past, but new investigations continue to provide surprising insights into the excitation and decomposition of this polyatomic molecule. Excitation of CH_3I at 193.3 nm creates a Rydberg state which may then predissociate or fluoresce.[1,2,3] A previous photofragment translational spectroscopy (PTS) study suggested that after excitation to the (E,1){2} Rydberg state predissociation occurs solely to the (E,1) repulsive state , correlating with excited $I(^2P_{1/2})$ atoms and electronic ground state methyl radicals with υ_2 umbrella mode excitation.[1] We have recently performed PTS studies of CH_3I photodissociation with much improved sensitivity and resolution. The data indicate significant υ_1 symmetric stretch excitation, previously unobserved in the photodissociation of a symmetric top molecule. In addition, it was found that Rydberg excitation leads to C-H bond fission, which was previously only known to occur at wavelengths below 185 nm.[4]

These measurements were performed with a high resolution fixed source rotating detector molecular beam apparatus[5] modified for the production of intense pulsed photolytic atom and radical beams for reactive scattering studies. A skimmed pulsed beam of neat CH_3I at stagnation pressures of 8-45 torr was crossed at 90 degrees with the 193.3 nm ArF output of a Lambda Physik excimer laser. Recoiling photofragments were detected at 90 degrees relative to the molecular beam after travelling 39.1 cm via an electron bombardment ionizer/quadrupole mass spectrometer. The flight time of neutral dissociation products was measured by a multichannel scaler with .15 μsec time resolution. The velocity resolution of the apparatus is $\Delta v/v = 2\%$.

The methyl radicals produced by C-I bond fission yield signal at m/e=15,14,13,12 and 1. The m/e=15 TOF spectrum in fig. 1(a) shows a progression of features which we assign to the υ_1 symmetric stretching mode of CH_3 based on their spacing, (ca. 3000 cm^{-1}). The width of these peaks is due to the excitation of υ_2 umbrella motion,

as well as some rotational excitation of CH_3. Based on the time of arrival of the fastest CH_3, one can conclude that there is 100% $I(^2P_{1/2})$ production in the C-I bond fission channel, in accord with the previous PTS study.[1] However, this result contradicts the recent laser gain vs. absorption measurements which indicated only 70% $I(^2P_{1/2})$ production[6]. The polarization dependence indicates that the transition moment lies perpendicular to the C-I bond as Van Veen, et.al. have shown.[1] The m/e =14 TOF spectrum shows that the features assigned to vibrationally excited methyl radicals are enhanced by ca. 20% relative to $\upsilon_1=0$, indicating preferential ionization of these radicals to $CH_2^+ + H$. The overall signal at m/e =14 was 30% of that at m/e =15. At higher laser powers a broad underlying component appeared at m/e =14, which was due to CH_2 produced by sequential photodissociation of $CH_3 \rightarrow CH_2 + H$. This feature was also observed in the m/e=1 daughter ion spectrum of CH_3, CH_2, and CH, as the fit of the slow signal in figure 1(b) shows. Fig.1(a) shows the forward convolution[7] fit to the data, decomposed into the contributions for the υ_1 states, and, for $\upsilon_1=0$, the υ_2 contributions. The fundamental of the υ_1 mode has only recently been observed[8], and to the best of our knowledge, this marks the first observation of the higher overtones of this mode. Our preliminary estimate for the υ_1 vibrational distribution is $\upsilon_1=0$, 57%; $\upsilon_1=1$, 29%; $\upsilon_1=2$, 7%; $\upsilon_1=3$, 5%; $\upsilon_1=4$, 2%. The υ_2 distribution[9] used for $\upsilon_1=0$ was $\upsilon_2=0$, 11%; $\upsilon_2=1$, 35%; $\upsilon_2=2$, 21%; $\upsilon_2=3$, 18%; $\upsilon_2=4$, 9%; $\upsilon_2=5$, 3%; $\upsilon_2=6$, 2%, with an average rotational energy per state of .43 kcal/mol. This assignment leads to an upper bound to the C-I bond dissociation energy in CH_3I of 55.3 $\pm$ 0.3 kcal/mol. These results indicate that the previous assignment of the first two features in the TOF spectrum to a bimodal distribution of the υ_2 bending mode is incorrect[1].

The TOF spectrum of m/e=1 in fig. 1(b) shows a fast peak due to primary C-H bond fission. The slow peak is the sum of the m/e =1 fragments of CH_3, as mentioned above. The power dependence of C-H bond fission is nearly identical to that of the C-I bond fission channel. At laser fluences above 10 MW/cm^2 a fast broad signal due to the H atoms from the sequential photodissociation of $CH_3 \rightarrow H + CH_2$ mentioned above was observable as well. The signal was also shown to be linear with pressure, indicating that dimers were not responsible

for this feature. Polarization studies show that the C-H bond fission channel has a much lower anisotropy, which is consistent with C-I bond excitation followed by electronic energy transfer and fission of one of the three C-H bonds. The quantum yield for this channel is ca. 3%. The data yields an upper bound to the C-H bond energy in CH_3I of 101 ± 1 kcal/mol.

This study shows that a detailed understanding of the photodissociation dynamics of CH_3I must take into account dissociation pathways other than simple C-I bond fission with υ_2 excitation. We have also observed lesser quantities of C-H stretch excitation in the n -> σ^* repulsive state photodissociation of CH_3I at 248 nm and CH_3Br at 193 nm[10]. These results may indicate that the nascent product state distribution is governed by the dynamics of the repulsive energy release on the dissociative surface, rather than being dictated by the details of the predissociative mechanism, as previously postulated[1]. The observation of C-H bond fission is especially interesting, as this bond is almost twice as strong as the C-I bond. This channel appears to be correlated with the relatively long lived Rydberg state excited. No C-H bond fission is observed in the 193 nm photolysis of CH_3Cl or CH_3Br[10], indicating that direct excitation of the CH_3 moiety is probably not responsible for C-H bond fission as it presumably is at shorter wavelengths[4]. C_2H_5I, which also predissociates from a Rydberg state, shows a primary C-H bond fission channel[11]. A full account of this work, including isotope effects in CD_3I, is in preparation. The advantages to be gained from high sensitivity universal detection of low mass photofragments, such as quantum state resolution and more accurate bond energies, are clearly shown by this study.

Acknowledgement:

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of The U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1]G. N. A. Van Veen, T. Baller and A. E. DeVries, Chem. Phys. **97**, 179 (1985)

[2](a) D. J. Donaldson, V. Vaida and R. Naaman, J. Chem. Phys. **87**, 2522 (1987)

(b) S. P. Sapers, V. Vaida and R. Naaman, J. Chem. Phys. **88**, 3638 (1988)

[3]K. Lao, M. D. Person, T. Chou and L. J. Butler, submitted to J. Chem. Phys.

[4]M. R. Levy and J. P. Simons, J. Chem. Soc. Faraday Trans. 2 **71**, 561 (1975)

[5](a) Y. T. Lee, J. D. McDonald, P. R. LeBreton and D. R. Herschbach, Rev. Sci. Instrum., **40**, 1402 (1969)

(b) R. K. Sparks, Ph. D. thesis, University of California, Berkeley, 1979.

[6]W. P. Hess, R. Naaman and S. R. Leone, J. Phys. Chem., **91**, 6085 (1987)

[7]X. Zhao,G. M. Nathanson and Y. T. Lee, in preparation.

[8]P.L. Holt, K. E. McCurdy, R. B. Weisman, J. S. Adams, and P. S. Engel, J. Chem. Phys. **81,** 3349(1984)

[9]The υ_2 energy levels were taken from H. W. Hermann and S. R. Leone, J. Chem. Phys. **76**, 4759 (1982)

[10] Work in preparation.

[11] Work in preparation.

Figure Captions

Fig. 1(a); The m/e = 15 TOF spectrum of CH_3. The solid line is the summed fit to the data. The heavy broken curves are the forward convolution fits to the υ_1 vibrational distribution with arrows marking the peak positions for υ_1 = 0-4. The light broken curves show the υ_2 distribution used to fit υ_1 = 0.

Fig. 1(b); The m/e = 1 TOF spectrum. The sharp peak at ca. 25 μsec is due to the primary C-H bond fission channel. The fit to the m/e=1 daughter ions of CH_3, CH_2, and CH shows a broad underlying feature from sequential methyl radical photodissociation as well as enhanced signal from the υ_1 excited methyl radicals, similar to m/e=14 spectra. Both spectra were averaged over 100,000 laser shots.

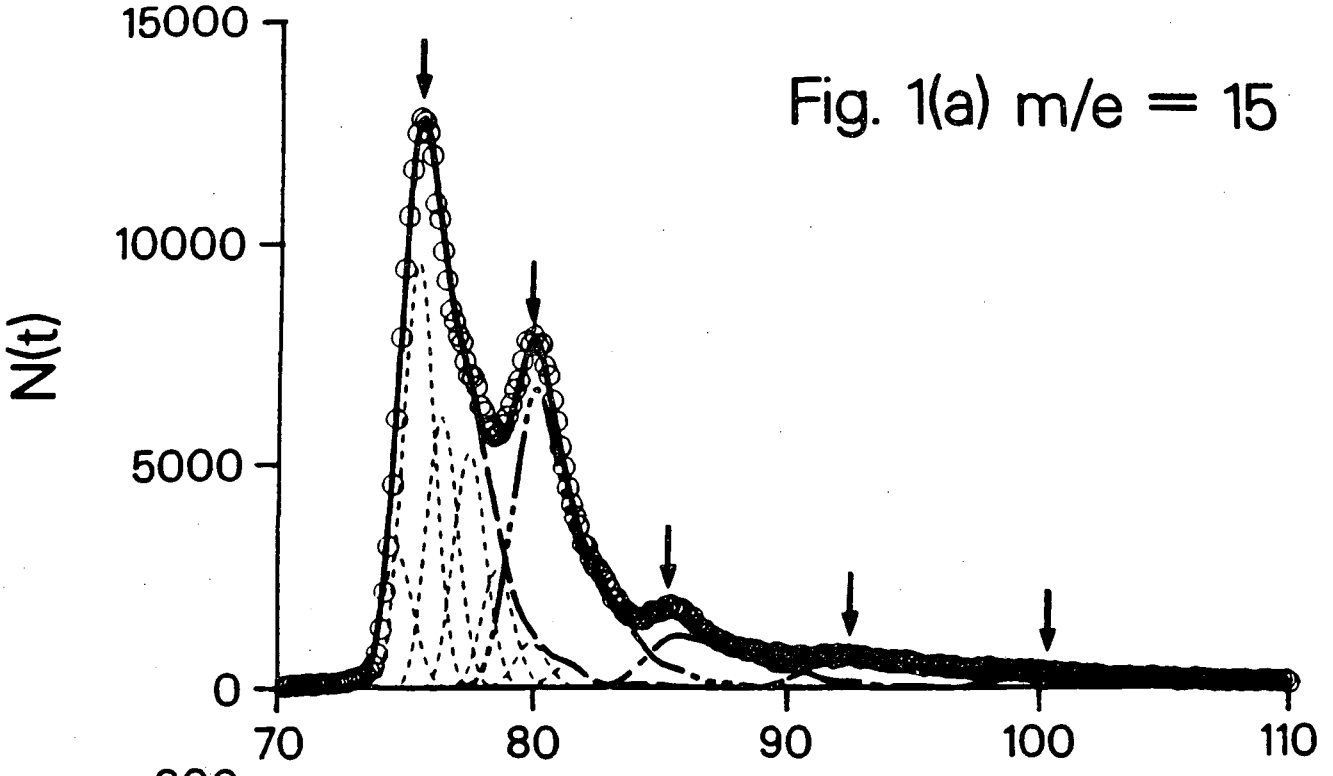


Fig. 1(a) m/e = 15

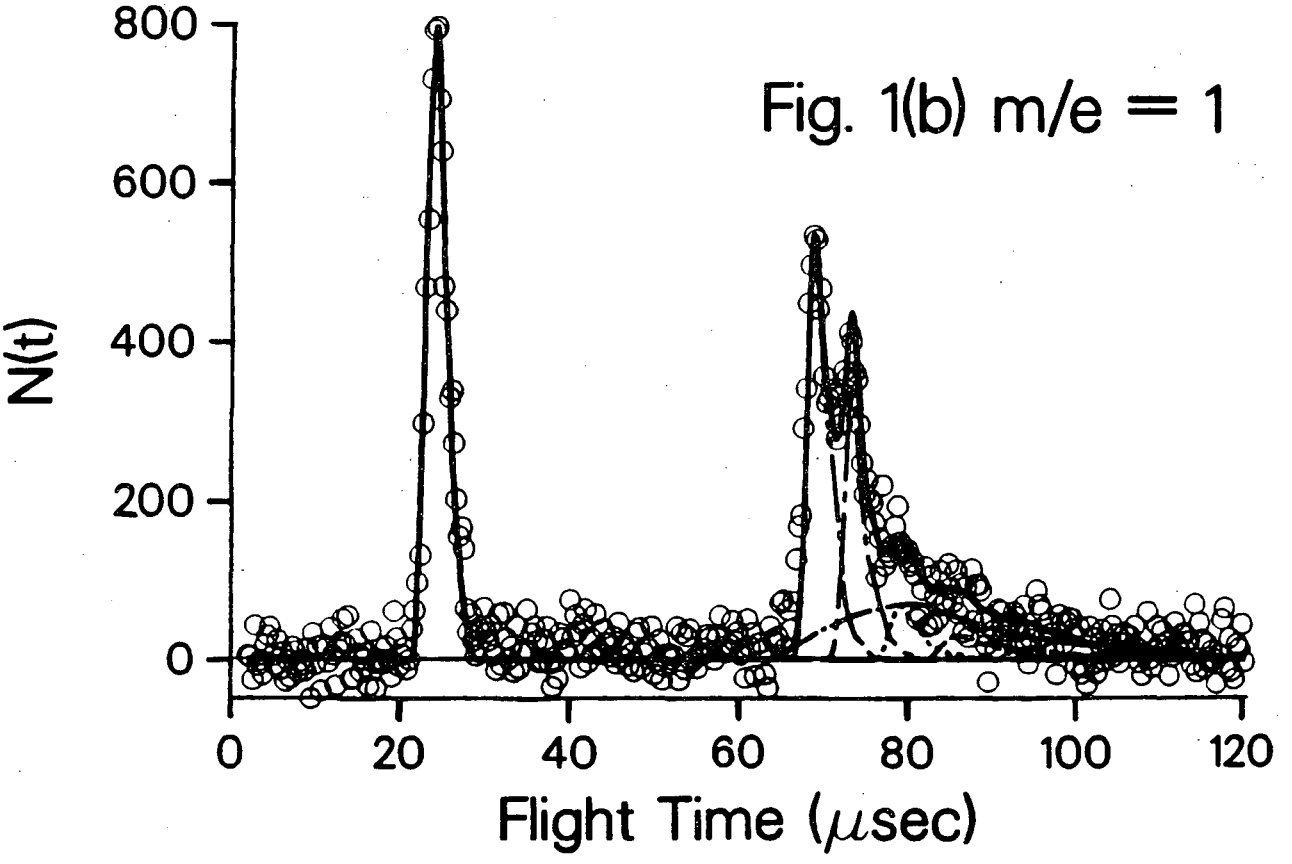


Fig. 1(b) m/e = 1

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720